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THE

PHYSICAL REVIEW

THE ELECTRON DISTRIBUTION OF MAGNESIUM OXIDE

By E. O. Wollan

Ryerson Physical Laboratory, University of Chicago

(Received March 16, 1930)

Abstract

The *intensity of x-rays reflected* from powdered crystals of magnesium oxide was measured for all lines out to $\theta = 45°$. The values of the structure factor, F, were calculated and plotted against sin θ. Using the values of F from this curve as coefficients in Compton's Fourier series, the *radial electron distribution for the atoms of magnesium and oxygen* was determined. The electron distribution curves for these atoms are very similer to Havighurst's curves for sodium chloride and sodium fluoride. Although it has been generally conceded that crystals of the magnesium oxide type are polar in form, the data here included are more in line with their being non-polar crystals. However, it is not believed possible from x-ray reflection data to prove definitely this point.

Introduction

THE intensity of reflection of the K_α line of molybdenum has been measured for powdered crystals of magnesium oxide. The structure factor curves have been calculated, and the electron density in the crystal and the radial electron distribution in the atoms of magnesium and oxygen have been determined, using the Fourier Series worked out by A. H. Compton.[1] Besides being able to determine the distribution of the electrons in the atoms, the total number of electrons associated with each point of the space lattice can thus be found. This should make it possible to decide whether the crystal is in a polar or non-polar form. In the work of Bragg, James, and Bosanquet, sodium chloride was concluded to be polar and Havighurst has concluded that several crystals with which he worked were of this form. In general the evidence seems to favor this view for crystals of the sodium chloride type, but it can hardly be said to be conclusive.

Magnesium oxide has been chosen for analysis, not only for the interest in determining the electron distribution in the atoms of magnesium and oxygen, but also because it is a very suitable substance for showing the state of ionization of the atoms in the space lattice.

[1] A. H. Compton, "X-Rays and Electrons."

Experimental Procedure

The accuracy with which intensity measurements can be made with powdered crystals is limited to some extent by the difficulty of obtaining a strictly homogeneous beam of x-rays of sufficient intensity. It was found that the method used by Havighurst[2] was most suitable for obtaining accurate results, especially at large angles, where the intensity is very weak. This method is essentially that first used by W. H. Bragg,[3] and consists in utilizing the focussing effect of randomly oriented crystals pressed into a flat plate, and the use of zirconium oxide filters for cutting out the K_β and K_γ lines and a greater part of the general radiation. The arrangement of the author's apparatus is shown in Fig. 1. A molybdenum target x-ray tube was operated at a potential of 35 kv and 35 m.a., supplied by a transformer with full wave rectification.

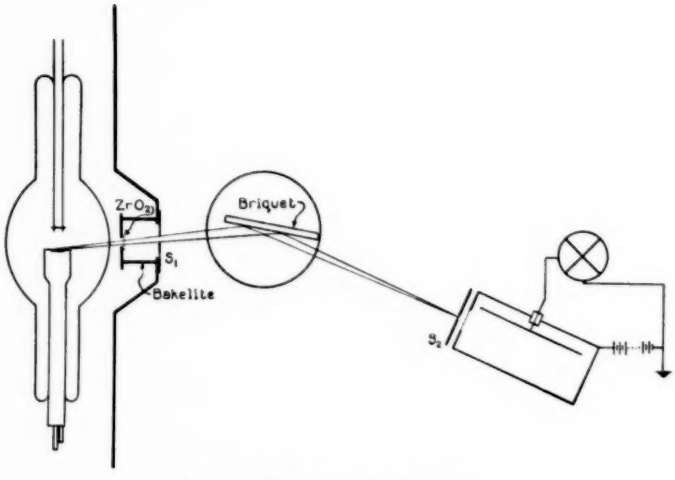

Fig. 1. Diagram of apparatus

The pure magnesium oxide powder was pressed into a brass ring two inches in diameter. The mass per cm^2 of the powder was made just great enough for practically total absorption of the K_α lines of molybdenum. In this way some of the general radiation of shorter wave-length was not effective in scattering and increasing the continuous background.

The slits used in front of the ionization chamber were accurately measured to be of such width that when the briquet was moved through some predetermined increment of arc (generally five to ten minutes) the slit, S_2, moved through its own width. In this way all the reflected energy was received in the ionization chamber.

The ionization current was measured with a Compton electrometer, having a sensitivity of from five to ten meters per volt. The rate of deflection of the electrometer needle was taken at each increment of arc corresponding

[2] R. J. Havighurst, Phys. Rev. **28,** 832, (1926).
[3] W. H. Bragg, Proc. Phys. Soc. London, **33,** 222 (1921).

to the width of the slit, S_2. The reciprocals of these readings were plotted as ordinates against the angle θ and the intensity of the line was taken as proportional to the sum of the ordinates above the base line. If the increments are small the intensity is also proportional to the area under the curve. Different widths of slits, S_2, were found to give results in satisfactory agreement.

Table I, column three, gives the average of the relative intensity measurements where the intensity of the (200) reflection has been taken equal to 100.00. The measurements have been extended to about $\theta=45°$. This is as far as the spectrometer could conveniently be used.

TABLE I. *Measured values of F for magnesium oxide.*

Plane	Sin θ	Rel. Int.	F
111	0.1464	8.55	2.92
200	0.1691	100.00	13.40
220	0.2390	55.10	10.15
311	0.2804	5.80	2.78
222	0.2929	15.20	8.20
400	0.3380	6.00	6.94
331	0.3684	2.53	2.51
420	0.3780	13.20	5.92
422	0.4140	8.72	5.35
511	0.4392	1.07	1.73
333			
440	0.4782	1.71	4.00
531	0.5000	0.83	1.41
600	0.5071	3.31	3.78
442			
620	0.5344	1.84	3.22
533	0.5542	0.25	1.29
622	0.5606	1.30	3.00
444	0.5856	0.37	2.90
551	0.6036	0.19	0.90
711			
640	0.6095	0.89	2.60
642	0.6324	1.40	2.52
553	0.6492	0.16	0.71
731			
800	0.6762	0.12	2.21
733	0.6918		
644	0.6970	0.80	2.05
820			
822	0.7172	0.48	1.86
660			

STRUCTURE FACTOR DETERMINATIONS

Darwin[4] and A. H. Compton[5] have derived equations which relate structure factor and the integrated intensity of x-rays reflected from powdered crystals.

When the relative intensity measurements have been made by reflection from a briquet of powder as they were in this case, the equation for calculating the relative values of the structure factor, F, takes the simple form

[4] C. G. Darwin, Phil. Mag. **43**, 827, (1927).
[5] A. H. Compton, Phys. Rev. **9**, 29, (1917).

$$F^2 = \frac{P_s}{j} \frac{\sin\theta \sin 2\theta}{1+\cos^2 2\theta} \tag{1}$$

where P_s is the intensity of the reflected beam measured on some arbitrary scale, j is the number of planes cooperating in producing the intensity P_s and 2θ is the angle between the primary and the reflected beam. F^2 is the square of the structor factor in which the Debye[6] temperature factor, $\exp\left[(b^2\sin^2\theta)/\lambda^2\right]$, is included. The reasons for the inclusion of the Debye factor in the value of F have been pointed out by Havighurst.[2]

The relative values of F can be placed on an absolute scale by comparing the intensity of some line of the substance to be analyzed with the intensity

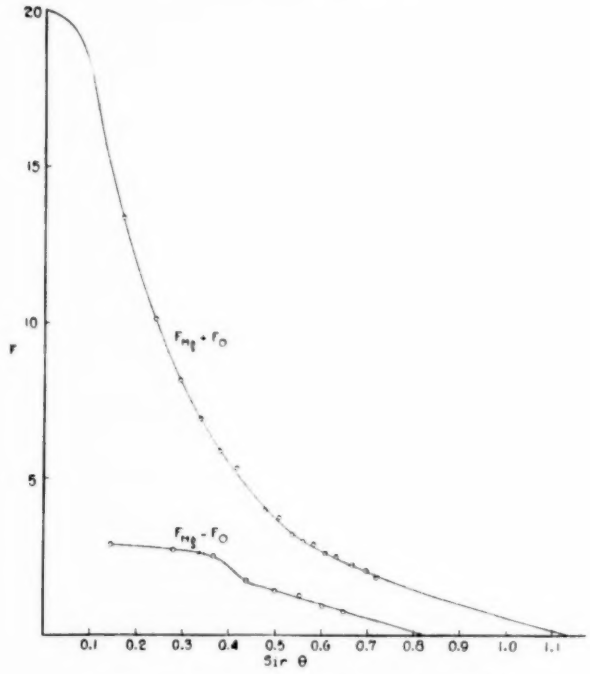

Fig. 2. Structure factor curve for MgO.

of a line of a substance for which the absolute value of F has been directly determined. The absolute value of F for the (220) reflection of sodium chloride has been measured by James, Bragg and Bosanquet[7] on single crystals, and corrected for secondary extinction. Their value of $F=15.75$, has been used as a standard for placing the relative F values of magnesium oxide on an absolute basis.

Table I, column IV gives the absolute values of F for all the lines measured, where F (220) was found equal to 10.15 by comparison with the same reflection from sodium chloride.

[6] P. Debye, Verh. d. D. Phys. Ges. **15,** 678, (1913).

[7] W. L. Bragg, James, and Bosanquet, Phil. Mag. **42,** 1, (1921).

Fig. 2 shows the F curves plotted from the above values of F. The upper curve is due to even order reflections and corresponds to $F_{Mg}+F_O$, while the lower curve corresponds to $F_{Mg}-F_O$. The values of F for the separate atoms can be found from the relations

$$F_{Mg} = \tfrac{1}{2}(F_{Mg}+F_O) + (F_{Mg}-F_O) \text{ and}$$
$$F_O = \tfrac{1}{2}(F_{Mg}+F_O) - (F_{Mg}-F_O). \qquad (2)$$

Since magnesium and oxygen are bivalent and have atomic numbers of 12 and 8, respectively, the ions would have 10 electrons each. This means that for ions the lower F curve is dependent on the different electron distributions and not on the number of electrons in the two ions. If the scattering centers are neutral atoms this curve would be a function of both the distribution and the number of electrons.

Electron Distribution Curves

For the determination of the radial electron distribution curves the equation derived by Compton was used. This is a one dimensional Fourier series and much easier to evaluate than the three dimensional series of Duane. The series has the form

$$U = \frac{8\pi r}{D^2} \sum_1^\infty nF_n \sin \frac{2\pi nr}{D} \qquad (3)$$

where U is equal to the number of electrons per Angstrom and r is the distance from the center of the atom in Angstroms. If both sides of this equation are multiplied by dr and integrated from 0 to $D/2$ one gets an expression for Z, the total number of electrons in the atom included between these limits,

$$Z = -2\sum_1^\infty (-1)^n F_n. \qquad (4)$$

In calculating the electron distribution curves for magnesium and oxygen, spherical symmetry has been assumed in the atoms, and the values of F were read directly from the F curves, assuming a grating space of 2.5A for the sake of convenience in calculations. This gives a series of only seven terms, but it was found that the distribution in the K and L shells was only very slightly different if a larger number of terms were used.

Table II. *Values of F from F-curves on basis of D=2.5A.*

Indices	Sin θ	$(F_{Mg}+F_O)$	$(F_{Mg}-F_O)$	F_{Mg}	F_O
111	0.142	15.00	2.92	8.96	6.04
222	.284	8.40	2.76	5.58	2.82
333	.426	5.10	2.00	3.55	1.60
444	.568	2.94	1.14	2.04	0.90
555	.710	1.94	0.44	1.19	0.75
666	.852	1.24	0.00	0.62	0.62
777	.994	0.60	0.00	0.30	0.30

Table II gives the values of $F_{Mg}+F_O$ and $F_{Mg}-F_O$ which have been taken from the F curves of Fig. 2 and the values of F_{Mg} and F_O, which have been calculated with the aid of Eq. (2). Using these values of F as coefficients in the series 3, given above, the electron distribution curves of magnesium and oxygen have been plotted in Figs. 3 and 4.

Magnesium

Fig. 3 shows the curve for the radial electron distribution in magnesium. The area under the curve corresponding to the K and L shells is about 9.5 electrons, unless a part of the adjoining hump is included. If the distribution is calculated on the basis of $D=5.00$A the area under this part of the curve is 10 electrons and its distribution is very nearly the same with a slightly better resolution of the hump at $r=0.5$A. The distribution in these shells is very similar to Havighurst's[8] curves for sodium in NaCl and NaF, except that in this case the average distance of the electrons from the nucleus is less.

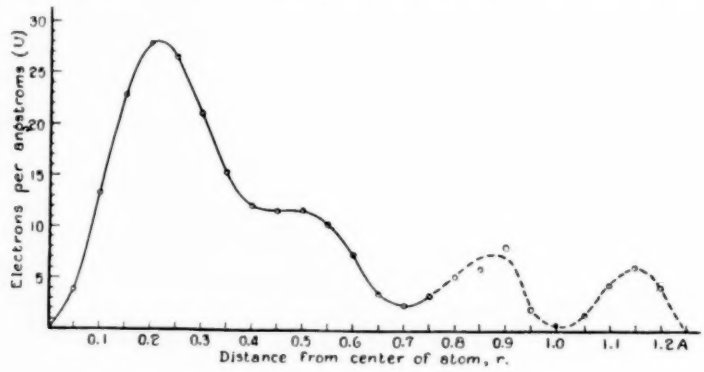

Fig. 3. Electron distribution in Mg.

This could be expected from the fact that magnesium has a higher atomic number and also that the grating space of Mg is less than for either of the other two substances mentioned.

In this curve there is also an indication of the two valence electrons, and these, as might be expected, are more loosely bound than the other electrons. Little significance can be placed in the positions of these humps, however, since they are not the same when calculated on the basis of $D=5.0$A.

The total number of electrons in the atom, according to this analysis is 11.50. This is the area under the curve and also the value as given in Table II, calculated from Eq. (4). In all cases the area under the curve checks the value from Eq. (4) as, of course, should be the case if no error is made in working out the Fourier series. The existence of only 11.50 electrons using the F values corresponding to $D=2.5$A and 11.04 electrons for $D=2.424$A indicates that some of the electron atmosphere is at a distance greater than

[8] R. J. Havighurst, Phys. Rev. **29**, 1, (1927).

$D/2$ from the nucleus, beyond which the series does not hold, since it drops to zero at this value.

Oxygen

Fig. 4 shows the radial electron distribution curve for oxygen. Here the electron shells in oxygen have areas corresponding to 3, 3.5 and 1.5 electrons with a small erratic variation near $D/2$. The fact that the humps do not represent an integral number of electrons may be due to experimental error,

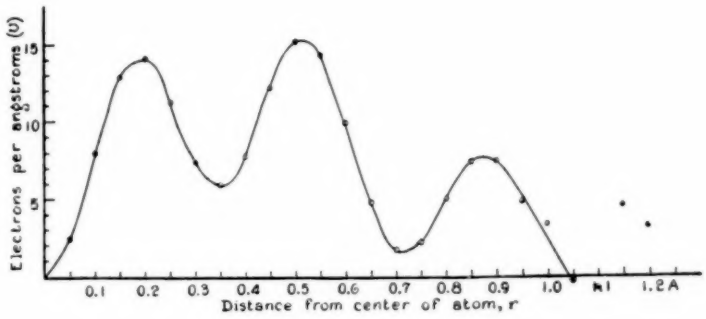

Fig. 4. Electron distribution in O.

but there is no reason, from the idea of elliptic and interpenetrating orbits, that the distributions should be made up of humps representing integral numbers of electrons.

The total area under the curve is equal to 8.7 electrons, which also checks the value in Table II, as calculated from Eq. (4). This curve for oxygen closely resembles Havighurst's curve for fluorine.

Electron Density in the MgO Crystal

Compton has derived a series which represents the number of electrons in a plane at any height above some atomic layer. This series has the form

$$P = \frac{Z}{a} + \frac{2}{a} \sum_{1}^{\infty} \left(F_n \cos 2\pi n \frac{z}{a} \right) \tag{5}$$

where P is equal to the number of electrons per Angstrom, z is the distance above the reference plane in Angstroms, and Z is the total number of electrons per molecule of the substance.

Using the values of F_{111}, F_{222}, etc., given in Table I and the value of F_{666} extrapolated from the F curve, as coefficients in this series and plotting P against z/a, one gets the curve shown in Fig. 5.

It will be noticed that the electron density does not fall to zero between the atoms. This means that the atoms overlap, and in order to tell how many electrons belong to each atom it is necessary to extrapolate the curve of one atom into the space of the other. This, in general, can be only a good guess; but in this case there is considerable difference in the size of the humps, and the most obvious extrapolation would be to give magnesium more electrons

than oxygen. In Fig. 5 extrapolations have been made for the two extreme cases of the neutral atom and the ion. The broken line shows how the curve can be extrapolated to give Mg 12 electrons and oxygen 8 electrons, while the dot and dash line gives the ions with 10 electrons each. From the fact that the radial electron distribution curves for magnesium do not contain 12 electrons between 0 and $D/2$, however, one is led to the conclusion that the valence electrons of magnesium spend part of the time nearer to the nucleus of oxygen than to that of the magnesium atom. It is, however, probable that the distribution for large values of r in the radial distribution

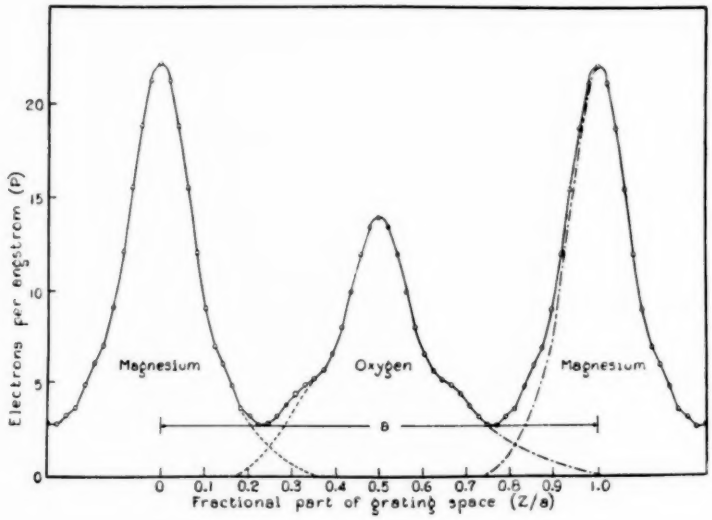

Fig. 5. Electron density in MgO.

curves, is no more reliable than a logical extrapolation of the curves in Fig. 5.

Using the table of F values worked out by Havighurst as coefficients in series 4, the total number of electrons associated with the atoms in various crystals has been determined and the results are shown in Table III. It will be seen that the analysis of these data by the use of Compton's series leads to no definite conclusions regarding the state of ionization of the atoms in the crystals considered.

TABLE III.

Mg		O	
$D=$ 2.5A	$Z=11.52$	$Z=$ 8.70	
2.424A	$Z=11.04$	$Z=$ 8.42	
5.00A	11.56	8.34	
	Havighurst's Data		
NaCl	NaF	CaF_2	LiF
$Z_{Na}=10.82$	$Z_{Na}=10.48$	$Z_{Ca}=19.04$	$Z_{Li}=1.42$
$Z_{Cl}=17.54$	$Z_F=$ 9.12	$Z_F=10.46$	$Z_F=8.38$

Conclusion

There seems to be fairly good agreement in the data of different observers for the distribution of the electrons in the K and L shells of various atoms. For magnesium there is no overlapping of these shells for neighboring atoms. In the shells of larger radius, where there is overlapping of the electrons for the two or more atoms considered, it is quite likely that the analysis of the distribution is less reliable.

From the data at hand, one is hardly justified in drawing definite conclusions regarding the location and the behavior of the valence electrons in the atoms of crystals. To say that an atom is ionized in the crystal presumably means that the electrons are revolving about the nucleus of the other atom. Since a large portion of each atom overlaps its neighbor, this implies that the analysis can detect whether an electron scattering at a point near the nucleus of one atom is actually revolving about the nucleus of the other. This can, at best, be only a good guess as to what is actually occurring.

The calculation of the distribution of diffracting power in some direction in the crystal is considerably more straightforward. Hence, a curve of the type of that shown in Fig. 5 would be more reliable than the radial distribution curves. In the case of magnesium oxide it would be easier to extrapolate this curve to give 12 and 8 electrons to the atoms of magnesium and oxygen, respectively, than to make an extrapolation giving these atoms each 10 electrons.

Since there is a considerable amount of overlapping of the neighboring atoms, it would be more reasonable to conclude from the data at hand that the valence electrons are shared by the atoms of magnesium and oxygen and that neither of the conclusions regarding the existence of ions or neutral atoms in the points of the crystal lattice is altogether correct.

In conclusion, the writer wishes to express his appreciation to Professor A. H. Compton for his helpful suggestions throughout the work.

PREDISSOCIATION OF DIATOMIC MOLECULES FROM HIGH ROTATIONAL STATES

By D. S. Villars and E. U. Condon
University of Minnesota, Minneapolis

(Received March 12, 1930)

Abstract

Instability of molecules in high rotational states, as observed especially in HgH and AlH, is a phenomenon whose quantum-mechanical explanation is closely analogous to that of the radioactive disintegration of atomic nuclei. The heat of dissociation of AlH from its normal state is estimated to be 3.07 volts.

THE observations of Henri[1] and his school, that certain band systems apparently pass progressively from a discontinuous to a continuous character in such a manner as to indicate that the emitting molecules lose their rotational quantization before they lose their vibrational quantization, has been ascribed to a "predissociation" by various writers. The generally accepted mechanism for this process is that proposed by Bonhoeffer and Farkas,[2] who assume, in accordance with quantum mechanics, that there may occur a radiationless transition of the molecule in a definitely quantized rotational and vibrational state, to another electronic state for which the same total energy places the molecule in the continuous energy range corresponding to dissociation. When the probability of transition from the quantized level to the dissociated state is high, the average life of the molecule may become less than a rotational period of the molecule so the corresponding band is diffuse. But there is an additional mechanism for predissociation which also is a consequence of quantum mechanics which has not been mentioned before, so far as we are aware.

It is known that the set of rotational quantum levels associated with the same vibrational quantum number may extend up to values of the total energy in excess of the amount necessary to dissociate the molecule in that electronic state. Such sets of rotational levels however do not extend upward indefinitely but are often observed to break off rather suddenly. In at least one instance, that of aluminum hydride, the last two or three levels broaden out so that lines involving them become faint because their energy is spread out more on the photographic plate. This phenomenon has been interpreted by Mulliken,[3] Hulthén,[4] and Ludloff[5] as due to an instability of the molecule arising from the high rotation. What has been lacking is an

[1] Henri, Photochemie (1919); Structure des Molécules (1925).
[2] Bonhoeffer and Farkas, Zeits. Phys. Chem. **134**, 337 (1927).
[3] Mulliken, Phys. Rev. **25**, 509 (1925).
[4] Hulthén, Zeits. f. Physik **32**, 32 (1925), **50**, 319 (1928).
[5] Ludloff, Zeits. f. Physik **39**, 526 (1926).

account of the nature of the instability and the reason that it sets in when it does.

Franck and Sponer[6] have advanced the view that the phenomena both of the sudden termination of such sets of rotational levels and the broadening of the last few levels, are to be interpreted as Bonhoeffer and Farkas have suggested. Oldenberg,[7] from classical ideas alone, has criticized this paper of Franck and Sponer. He points out that the potential energy governing the radial motion of a molecule that is rotating with quantum number, m, is equal to

$$U_m(r) = U_0(r) + \frac{h^2}{8\pi^2\mu}\frac{m(m+1)}{r^2}$$

where $U_0(r)$ is the potential energy for the non-rotating molecule and is determined by the electronic state. Since for large r, $U_0(r)$ becomes constant more rapidly than r^{-2} approaches zero, the function $U_m(r)$ is positive for large values of r and will show, for m not too great, a minimum followed by a maximum at greater nuclear separation. This behavior is illustrated by Fig. 1 which represents the curves (Morse[8]) for HgH.

The similarity of the curves with those that lie at the basis of quantum mechanics of radioactive disintegration[9] is evident. Hence the general properties of the wave equation which were so successful in that field are applicable here. The formula for the mean time of remaining essentially in the range of the periodic classical motion near the minimum, before going over into the range of the aperiodic classical motion extending from beyond the maximum to infinity, there developed for the atomic nucleus, is here applicable to the dissociation of molecules by rotation. We do not expect accurate results from it, both because it is based on an approximate integration of the wave equation, and because it requires an accurate knowledge (which we do not have) of $U_0(r)$ for the larger values of r. In principle, however, we have the means of inferring from the $U_0(r)$ curve, which is inferred from the energy levels, the exact maximum value of the rotational energy which can give levels effectively sharp in radiative transitions. These are the ones for which the mean life, τ, of the molecule before it "leaks" through the hump in the potential energy curve is large compared with 10^{-8} sec, which is the mean life needed to provide a sharp line in spectroscopic instruments of the resolving power actually available to experimenters.

Oldenberg has shown that there will be no trace of any discrete level structure for any value of m greater than the one for which $U_m(r)$ has a horizontal inflection point. (An *integral* value of m may not give a horizontal inflection point, m is regarded here as a continuous variable). He also mentions that owing to the existence of the so-called zero-point vibration energy the actual

[6] Franck and Sponer, Göttinger Nachr., p. 241 (1928).
[7] Oldenberg, Zeits. f. Physik **56,** 563 (1929).
[8] Morse, Phys. Rev. **34,** 57 (1929).
[9] Gurney and Condon, Phys. Rev. **33,** 127 (1929).

values of m will not extend this far. But there is another factor to consider: the level in question must be sufficiently below the maximum of the $U_m(r)$ that the mean life before leakage is large compared to the mean life before radiation. It is clear why the rotational levels associated with the second vibrational quantum state cannot extend as high as those associated with the

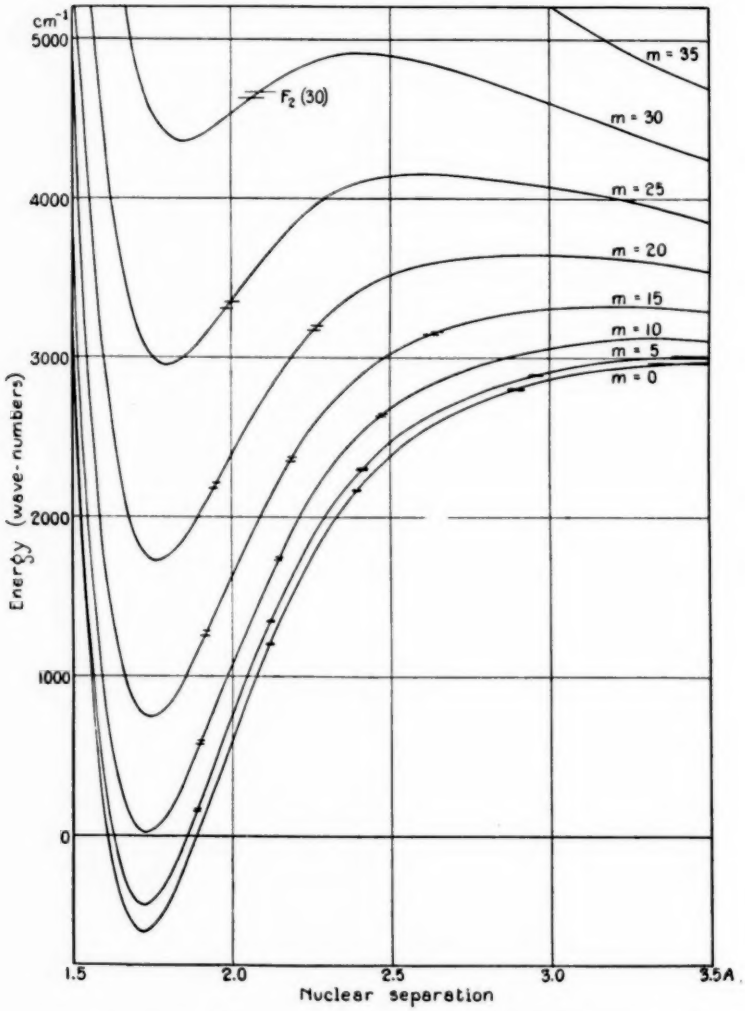

Fig. 1. Rotational vibrational (Morse) curves for HgH (normal $^2\Sigma$ state.) The designation $F_2(30)$ refers to the upper of the two doublet levels on the $m=30$ curve.

first; they are always higher above the minimum of the $U_m(r)$ curve because of the extra vibrational energy and therefore the requirement that they be sufficiently below the maximum of $U_m(r)$ can only be satisfied for smaller values of m. This behavior is nicely illustrated by the levels of HgH plotted by Franck and Sponer in their Fig 2.[6]

This behavior is also shown by the excited electronic state of AlH concerned in the band system studied by Eriksson and Hulthén.[10] Here only two vibrational levels are known so that the heat of dissociation cannot be found by the usual method of extrapolation of vibration levels, due to Birge and Sponer.[11] Fig. 2 shows the range of rotational energy associated with the zero and one vibrational levels of this electronic level. Comparing this figure with the analogous one for HgH, we do not hesitate to say that the dissociation energy for excited AlH must lie below the lowest fuzzy level and above the one quantum vibration level with zero rotation. This puts it probably within the range of the braces around "D" in the figure, that is,

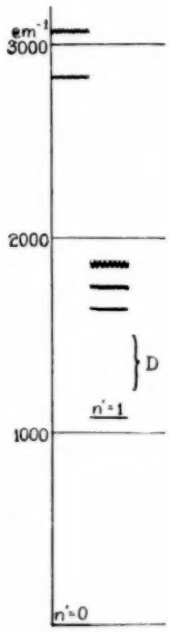

Fig. 2. Predissociation levels in the excited $^1\Pi$ state of AlH.

it is close to 0.17 ± 0.02 volts. This is the quantity called "y" in Table I of Mulliken's[12] study of band spectra of diatomic hydrides. Hence the heat of dissociation from the normal state is 3.07 volts. This is essentially the conclusion of Franck and Sponer, though from different theoretical considerations.

Oldenberg[13] is of the opinion that the radiationless transfers in the nuclear separation coordinate violate Franck's principle because they call for a fairly large "sudden" alteration in the nuclear separation. We feel that this is an attempt to push the Franck idea beyond the limits of its validity. The

[10] Eriksson and Hulthén, Zeits. f. Physik **34,** 786 (1925).
[11] Birge and Sponer, Phys. Rev. **28,** 259 (1926).
[12] Mulliken, Phys. Rev. **33,** 730 (1929).
[13] Reference 7, p. 573.

principle is simply an easily visualized rule describing approximately what quantum mechanics will predict. The connection with quantum mechanics has already been developed.[14] The principle has to do with the nuclear motions accompanying electron transitions and not with the nuclear motions when there is no change of electronic state.

A rough calculation for HgH was made, using a Morse function for $U_0(r)$,

$$U_0(r) = 2990 + 3592e^{-6.25(r-r_0)} - 7184e^{-3.125(r-r_0)},$$

where energy is measured in cm^{-1} and distance in 10^{-8} cm. The zero-point vibrational energy was arbitrarily taken as one-half the difference between the two lowest vibrational levels. The quantity ω_e was taken as 1528.8 cm^{-1}. These assumptions are somewhat arbitrary but are the best that can be made. The half-breadth of a line is given by

$$\Delta\nu/c = 1/4\pi\tau c,$$

(compare Pauli, Handbuch der Physik, vol. 23, p. 70). With the formula for mean life from Gurney and Condon[15], the half-breadth of the line with rotation quantum number thirty and zero vibration comes out to be 39 cm^{-1}. Actually this level gives rise to a sharp line, but a slight change in the form of the $U_0(r)$ curve, entering the exponent of the formula for τ will make it be sharp, so we conclude that insufficient knowledge of the $U_0(r)$ function does not justify further calculations at present.

[14] Condon, Phys. Rev. **32,** 858 (1928).
[15] Reference 9, p. 133.

NEW MEASUREMENTS ON THE FOURTH POSITIVE BANDS OF CARBON MONOXIDE

By L. B. Headrick and G. W. Fox
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(Received March 19, 1930)

Abstract

New measurements of that part of the fourth positive band system of carbon monoxide between 2174A and 1280A have been made from plates photographed with a one-meter vacuum spectrograph. Low voltage arc excitation was used. The densities of the band edges were determined from a microphotometric trace. A few new band edges lying below the fourth positive system are reported. In general the measurements here reported are in good agreement with the wave-lengths published by Birge.

Introduction

THE fourth positive band system of carbon monoxide extending from 2800A to about 1280A has been measured in parts by a number of investigators at different times. Birge[1] describes the work previous to 1926 and analyzes data taken by Deslandres, Bair, Duncan, Lyman and Leifson. Recently Estey[2] discusses the papers on CO subsequent to 1926 and reports new measurements on that part of the fourth positive system lying between 1970A and 2800A.

In the course of some work with a vacuum spectrograph, measurements were made on the part of the fourth positive system of CO lying between 1280A and 2174A. It seems advisable to report these results at this time to give a more complete set of new measurements for this important band system.

Experimental Details

The bands were photographed with a one-meter vacuum spectrograph of the design described by Sawyer.[3] Two plates were made; one of short exposure for microphotometer records and the other of longer exposure for wave-length determinations.

A low voltage arc in CO containing a trace of hydrogen was used to excite the bands. The gas pressure was 0.5 mm of mercury, current 10 to 12 m.a. and potential difference 22 volts. An enlargement of one of the plates extending from 2090A to 1150A is shown in Fig. 1. A microphotometric trace of the same plate, made on a Moll self-recording microphotometer is shown in Fig. 2. The densities of the band edges and lines given in Table II and

[1] Birge, Phys. Rev. **28,** 1157 (1926).
[2] Estey, Phys. Rev. **35,** 305 (1930).
[3] Sawyer, J.O.S.A. **15,** 305 (1927).

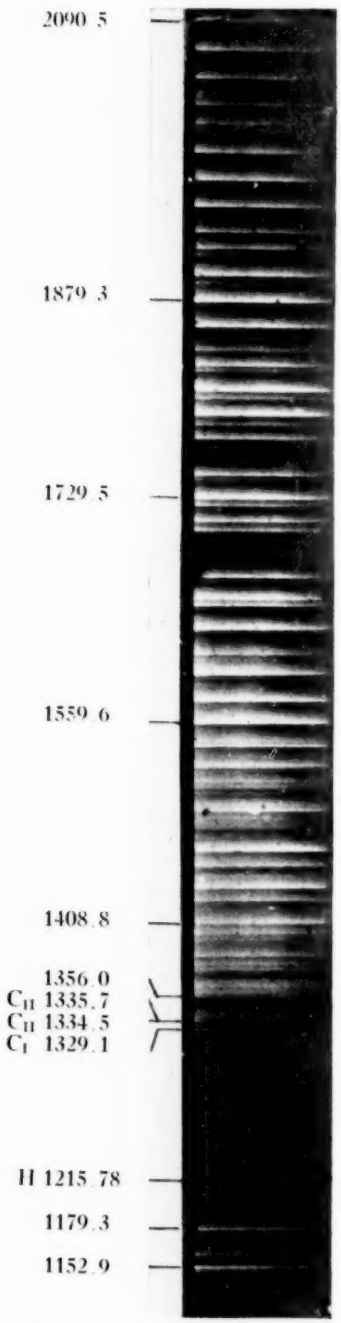

Fig. 1. The fourth positive band system of CO.

Fig. 2. A microphotometer record of part of the fourth positive band system of CO, from 2090.5A to 1280.6A. Including the hydrogen line 1215.78A, several carbon lines and bands of CO at 1179.3 and 1152.9A.

Table III were obtained from this trace by use of the relation,[4] density $=\log d/(d-h)$, where d is the total galvanometer deflection in the absence of a line and h is the height of the peak on the trace corresponding to a band edge or line.

The carbon line 2479.29 was used as a standard for the measurements of the bands from 2173.8A to 1595.8A. The hydrogen line 1215.78A was used as a standard for the measurements from the lower wave-length end of the plate up to 1611.5A. The measurements from the two standard lines overlapped for several bands near 1600A. The two measurements obtained in this way for the same edges checked within 0.2A.

The grating constant varied somewhat over the region photographed. The best values for it were previously determined experimentally by Dr. J. E. Mack. Table I gives these values for the regions over which they may be applied.

TABLE I.

Grating constant Angstroms/mm	Wave-length range
17.49	2332.2A−1970.0A
17.47	1970.0A−1729.5A
17.46	1729.5A−1597.4A
17.44	1597.4A−1025.7A

RESULTS

The measurements on the band edges, their densities as obtained from the microphotometer record, and their identification as assigned by Birge[1] are given in Table II. Some of the weaker band edges could not be measured on the plate but they appear on the photometer record in Fig. 2. A few new unidentified bands which apparently belong to the fourth positive system of CO are included in Table II.

TABLE II.

λ(IA)	ν (cm^{-1})	Density $\times 10^1$	n'	n''
2173.8	46002.8		5	13
2150.9	46492.8		4	12
2138.1	46770.9		7	14
2129.1	46968.9		3	11
2107.9	47439.7		2	10
2090.5	47835.0	0.5	5	12
2068.3	48348.7	0.7	4	11
2046.9	48854.4	0.5	3	10
2042.9	48949.5	0.3		
2034.9	49142.2	0.7	6	12
2026.3	49351.3	1.4	2	9
2012.4	49691.2	0.7	5	11
2006.4	49839.8	0.4	1	8
1990.8	50230.3	1.6	4	10

[4] Hughes and Lowe, Phys. Rev. **21**, 292 (1923).

TABLE II (*continued*).

λ(IA)	ν(cm⁻¹)	Density ×10¹	n′	n″
1970.0	50761.7	2.8	3	9
1950.0	51281.5	2.6	2	8
1930.6	51797.1	3.0	1	7
1918.0	52129.5	1.4	4	9
1912.8	52279.9	0.5	0	6
1897.8	52692.0	4.0	3	8
1879.2	53214.4	6.1	2	7
1859.3	53782.5	4.8	1	6
1850.1	54050.8	0.3	4	8
1841.3	54309.8	1.3	0	5
1829.9	54646.9	4.0	3	7
1827.6	54715.7	0.8	6	9
1810.8	55223.0	7.6	2	6
1804.9	55404.7	1.9	5	8
1792.4	55790.8	7.5	1	5
1784.9	56026.8	1.3	4	7
1772.9	56403.8	3.4	0	4
1747.1	57238.7	3.8	2	5
1743.5	57356.2	0.7	5	7
1729.5	57820.8	6.1	1	4
1723.7	58013.4	2.2	4	6
1712.2	58403.4	3.9	0	3
1704.8	58658.9	3.1	3	5
1684.9	59350.0	0.4	5	6
1669.7	59891.7	3.9	1	3
1647.8	60687.3	4.0	3	4
1629.6	61366.3	6.9		
1611.5	62055.9	3.1	4	4
1597.4	62603.7	6.9	0	1
1595.8	62665.3	1.6	6	5
1576.8	63421.6	7.1	2	2
1559.6	64120.6	7.0	4	3
1545.3	64712.8	3.5	0	0
1542.4	64835.7	6.9	3	2
1525.7	65542.0	5.3	2	1
1515.7	65977.9	2.5	7	4
1510.4	66206.3	1.8	4	2
1492.6	66997.2	6.0	3	1
1480.2	67556.6	1.5	5	2
1463.4	68333.3	9.0	4	1
1452.2	68859.6	4.9	6	2
1435.3	69671.4	6.4	5	1
1425.8	70136.5	4.7	7	2
1408.8	70981.4	4.8	6	1
1401.0	71378.1	2.5	8	2
1384.0	72256.9	2.7	7	1
1378.0	72566.8	1.5	9	2
1373.7	72796.1	0.9	11	3
1363.3	73350.4	1.1		
1356.0	73746.3	0.4	10	2
1316.0	75986.7	0.3		
1299.3	76965.7	0.2		
1280.5	78091.4	0.2		

In Table III are given the wave-lengths of the C_I and hydrogen lines which were used as standards to measure the band edges. A few other C_I and C_{II} lines which were used to check the measurements are also given in this table. Measurements of four strong unidentified band edges below the fourth positive system are included. Three of these band edges may be seen

on the microphotometric trace, one just to the left of the hydrogen line. The other two at the right of this line are marked. The fourth one at 1025.7A is not shown on the trace. This was the shortest wave-length edge observed.

TABLE III.

λ (IA)	ν (cm^{-1})	Density $\times 10^{1}$	Remarks
1335.7	74866.8	0.3	C_{II} line
1334.53	74932.2	0.2	" "
1037.02	96430.1		" "
1329.1	75238.9	1.0	C_{I} line
2479.29	40334.1		" "
1215.78	82254.5	1.6	Hydrogen
1228.2	81422.6	0.7	
1179.3	84793.9	2.8	band
1152.9	86733.3	3.3	edges
1025.7	97496.3		

These edges probably belong to the absorption systems of Hopfield and Birge,[5] corresponding to transitions from excited states, above those giving rise to the fourth positive system and the normal state.

[5] Hopfield and Birge, Phys. Rev. **29**, 922 (1927).

ABSORPTION BANDS OF AMMONIA GAS IN THE VISIBLE

By Richard M. Badger
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(Received March 4, 1930)

Abstract

The article describes an investigation of the absorption spectrum of ammonia gas in the visible region. At 5490A an absorption region was found which was too weak for a complete investigation with the means at hand. On a second band at 6474A measurements on 57 lines are given, and the structure of the band is discussed. These two bands are the fifth and fourth overtones of an ammonia band at 3μ. Some interesting alternations of intensity are pointed out, and comparison is made with other ammonia bands of the same harmonic series. Some features of other portions of the ammonia spectrum are discussed in connection with the bands here investigated.

Introduction

IT WAS recently shown by Badger and Mecke[1] that molecular band spectra of the vibration-rotation type, corresponding to higher members of a harmonic series with a fundamental in the infra-red, may be photographed in the near infra-red or visible regions with the large dispersion of a long focus grating. In the case particularly investigated (ammonia gas) it was found that a complexity of structure was revealed which could only be surmised from the existing investigations on bands lying further in the infra-red and beyond the reach of photographic methods.

Recently, information concerning the spectra of diatomic molecules has been accumulating at a very rapid rate, so that the more important features of this type of spectrum are now quite well understood. Our knowledge of polyatomic molecules is in a much less satisfactory state, and up to the present only relatively small portions of the complete spectrum originating in any molecule of this type have been submitted to anything like a complete analysis.

The study of the vibration-rotation type of band with the relatively high resolution permitted by photography seems to offer important possibilities in the solution of the general problem, and a program for the investigation of a number of the simpler polyatomic molecules by this method has consequently been undertaken.

In the case of certain molecules it has been found that different vibration-rotation bands of the same molecule may have a very different appearance, even in the case of bands of the same harmonic series. Theoretical reasons for this on the basis of symmetry considerations have been discussed by Hund.[2]

[1] Badger and Mecke, Zeits. f. phys. Chem. **5**, 333 (1929).
[2] Hund, Zeits. f. Physik **43**, 805 (1927).

One of the most interesting cases of the kind mentioned is found in ammonia, which is a relatively simple molecule and one whose spectrum might be expected to be capable of treatment. At 3μ there is a band which has been investigated by Stinchcomb and Barker[3] and has been interpreted by Dennison[4] as due to a molecular vibration in which the change of electric moment is perpendicular to the symmetry axis. The harmonics of this band are relatively strong as shown by Badger and Mecke,[1] who investigated the fourth and located the fifth members of the series. The two bands of the series which have been studied present considerable difference in appearance and have several features of which the explanation is not immediately evident.

It is the purpose of the investigation described in this paper, as a part of the general program mentioned above, to extend the investigation of this harmonic series to higher members with the expectation that a comparison of several bands, and especially of the intensity alternation of each, will lead to an understanding of the nature of the various rotational and vibrational levels involved.

Experimental Procedure

The ammonia gas used in the investigation was a synthetic product and was confined in a steel absorption tube 280 cm long, closed at the ends with plate glass windows. Gas pressures of from one to five atmospheres were employed, but increasing the pressure did not seem to have great advantage, probably due to a broadening of the absorption lines. The source of illumination was a tungsten lamp.

The majority of the exposures were made with a six inch grating of ten foot radius of curvature. This grating gives intense spectra in the first order in the red, and has great freedom from ghosts. Some exposures were also made using the second order of a twenty-foot grating.

When using the ten-foot grating the exposures were made on a process panchromatic film which was very contrasty and fine grained. The exposure times ranged from ten to thirty minutes. Development was carried as far as possible without introducing excessive developer fog. When using the second order of the large grating it was necessary to use a faster film, which unfortunately was less contrasty than the process film, so that only the stronger lines showed up in the exposures. An iron arc calibration spectrum was photographed on each of the films.

Since, at best, the absorption bands studied are very weak, and direct measurements on the films were difficult, as all but the most intense lines disappear under the microscope of a comparator, the following procedures were used in working up the results.

(1) Enlargements of several different films were made on contrast paper. Measurements were made on each with a scale, and the results compared.

[3] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).
[4] Dennison, Phil. Mag. **1**, 195 (1926).

(2) The best film (most contrasty, free from blemishes) was microphotometered and measurements made on the record plate.

(3) Enlargements from four of the best films were made on contrast film and superposed (see Oldenberg, Zeits. f. Physik, **58,** 722 (1929)) and measurements made on the resulting composite picture. It is remarkable how this procedure averages out small defects in the plates and intensifies lines which on a single plate would be pronounced doubtful.

TABLE I. *The ammonia band at 6474A.*

λ(A)	$\nu(cm^{-1})$	I	λ(A)	$\nu(cm^{-1})$	I
6419.5	15573.1	0	6472.4	15445.9	
			6474.0	15442.0	9
6422.2	15566.7	0	6474.7	15440.5	
6423.3	15564.1		6475.7	15438.2	
6425.5	15558.6	0	6478.8	15430.6	6
6426.5	15556.2	1	6479.6	15428.7	
6427.8	15553.1	?			
6428.6	15551.1	?	6483.2	15420.1	6
6429.7	15548.5	?			
			6485.3	15415.3	
6431.8	15543.4	1	6485.8	15414.0	?
			6486.9	15411.5	
6434.5	15536.9	5			
6435.6	15534.3		6488.5	15407.7	5
			6489.5	15405.2	
6438.2	15527.9	10			
			6492.4	15398.4	1
6442.5	15517.7	9			
			6494.9	15392.5	4
6446.2	15508.6	8	6495.9	15390.0	
6449.5	15500.9	7	6498.2	15384.6	?
6450.4	15498.6		6499.3	15382.0	7
6453.1	15492.1	2	6501.0	15377.9	?
			6501.8	15376.0	?
6455.4	15486.7	2			
			6506.6	15364.7	6
6457.4	15481.9	3			
			6510.9	15354.6	1
6460.1	15475.2	0			
6460.8	15473.7		6512.9	15349.8	3
6363.6	15466.9	0	6514.9	15345.1	?
6364.7	15464.4				
			6517.1	15340.1	?
6364.9	15463.7	0			
6365.6	15462.2		6519.9	15333.3	2
6367.9	15456.7	0	6522.7	15326.8	?
6368.2	15456.1				
			6525.9	15319.4	1
6370.3	15451.0	?			
			6528.0	15314.4	?
			6529.4	15311.2	?

EXPERIMENTAL RESULTS

In this work two absorption regions were investigated corresponding to the fifth and sixth harmonics of the band at 3μ. At 6474A a band was found

with a broad Q branch, an R branch with four intense lines and several rather weak ones, and several irregularly spaced absorption maxima in a P branch. The most distinguishing features of the band are the four strong lines of the R branch.

In the region at 5490A, evidences of absorption were obtained in all of a number of exposures. The absorption lines were so weak, however, as to be of the same order as non-uniformities in the emulsion of the film, and although the center of the absorption band seemed to lie at about 5490A, the Q branch could not be identified with certainty. Consequently no data are given for this band.

In Table I is given a summary of the measurements on the ammonia band at 6474A. The lines for which an intensity is given are well assured as real by several measurements. The lines designated by a point of interrogation are very weak and are possibly somewhat uncertain. Included in braces are broader regions of absorption which are incompletely resolved into lines, but have maxima of absorption at the wave-lengths given. They have possibly a more complex structure than that indicated. All of the lines in the spectrum are rather broad, but this does not seem to be due to a lack of dispersion or resolving power in the means employed, since the spectrograms taken with the second order of the 20 ft. grating showed no better resolution than those taken with the first order of the 10 ft. grating. To secure complete resolution of the lines one would probably have to work at very low gas pressures and a correspondingly long absorption path.

Discussion of the Results

In Figure 1 is given for purposes of comparison a diagrammatic representation of three of the ammonia bands of the series with fundamental at 3μ. In the case of the band at 6474A the curve is adapted from a microphotometer investigation of the best spectrogram obtained. The vertical lines represent the position of absorption maxima as taken from the various measurements. The dotted lines indicate the less certain maxima. The band at 7919A is reproduced from the work of Badger and Mecke[1] and the curve for the band at 3μ is adapted from the figure given by Barker and Stinchcomb.[3]

Below the first two bands is indicated a provisional arrangement of the lines into "series." Each series includes all the lines where one of the quantum numbers characterizing the rotational states, say τ, makes the particular transition $\tau' \rightarrow \tau''$, the other quantum number, say j, making all possible transitions (with the restriction of course that $\Delta\tau$ and $\Delta j = 0 \pm 1$). In the case of the two harmonic bands all of the intense lines, at least, fit into five of these series. Higher series may also be present but the lines of these will nearly coincide with those of the series given, the first and sixth series coinciding, and so on. For the band at 6474A the assignment is possibly in some cases ambiguous owing to incomplete resolution of the lines.

From the figure the following characteristic features are evident. First of all one may note that the bands at 7919A and 6474A include many double

lines with a separation of the two components which is perhaps constant within experimental error, since the resolution is not complete. In general it seems to be the weaker lines which are so resolved, and it is not impossible that the broadness of the stronger lines conceals a similar structure, though in a few cases the stronger lines are relatively sharp and apparently single.

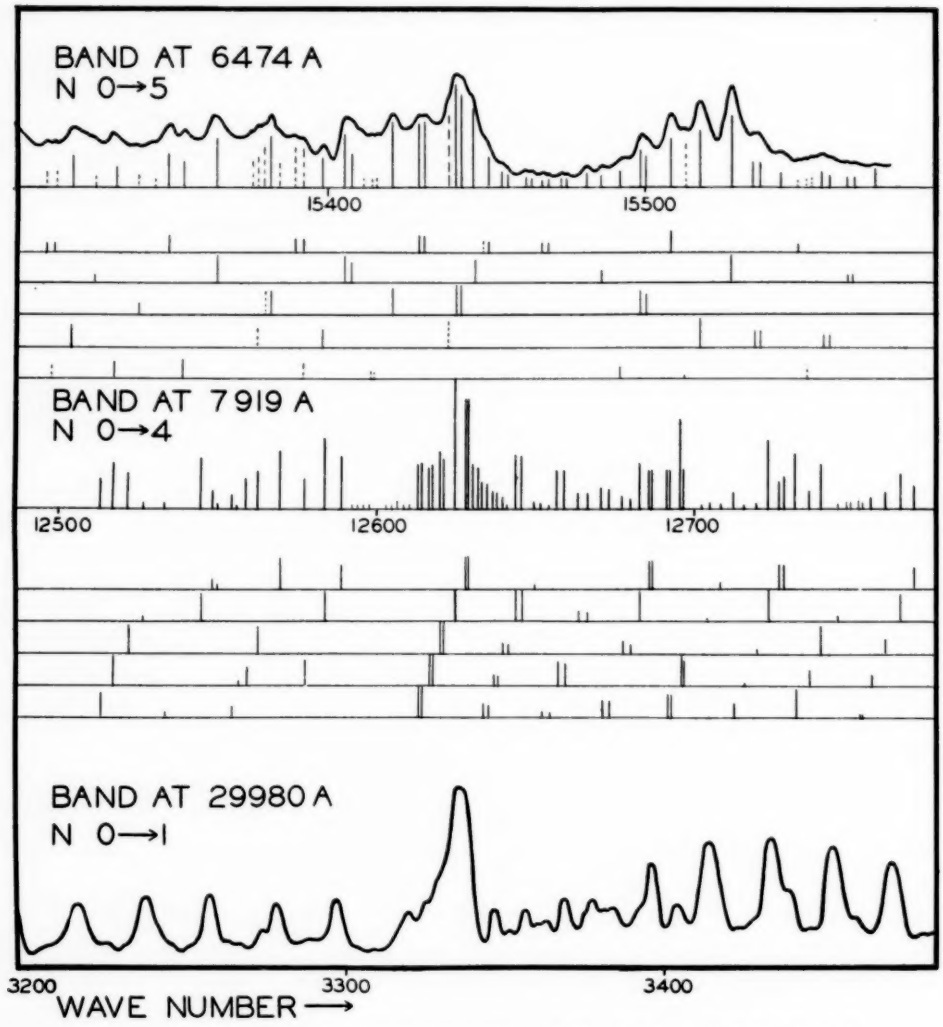

Fig. 1. Two harmonic bands of ammonia and the fundamental band at 3μ.

Badger and Mecke suggested as an explanation of the doubling that the ammonia molecule becomes slightly unsymmetrical as the amplitude of vibration increases. An alternative explanation has been offered by Barker[5] on the basis of a slight difference in the energy values corresponding to the symmetric and anti-symmetric eigenfunctions representing an oscillational state, this

[5] Barker, Phys. Rev. **33**, 684 (1929).

difference arising from the possibility of the nitrogen atom passing through the plane of the three hydrogen atoms. Barker interprets the bands here considered as due to an oscillation in which all the atoms of the molecule approach each other simultaneously. As the amplitude of this vibration increases the potential energy increase, as the nitrogen atom approaches the plane of the hydrogen, also rises, and the difference between energy levels corresponding to the two types of eigenfunction should decrease. Consequently the doubling of levels might be appreciable only in the lowest energy state, and the doubling of the bands would thus be nearly constant through the harmonic series. This is indeed in agreement with the data. However, it seems very questionable whether the bands here under consideration are due to the type of oscillation mentioned, first on account of the great intensity of transitions in which $\Delta\tau \neq 0$, and secondly on account of the convergence of the bands. An extrapolation of the harmonic series yields a dissociation energy of 6.0 volts, which is much less than that required for the complete separation of the molecule into its atoms (about 12 volts) which would result from the vibration in question. Dennison[4] in a treatment of the vibrations of the ammonia molecule by means of normal coordinates, concluded that the 3μ band arose from an oscillation perpendicular to the symmetry axis. But it is possible that even for this kind of oscillation one should expect a similar situation for the doubling of the vibrational levels.

It is striking that no very appreciable convergence in any series in any of the bands is observed. Furthermore, as one must expect from this fact, the spacing of the lines in a series is sensibly constant for all of the bands, having the approximate mean value 19.88 cm^{-1} for the band at 7919A and 19.74 cm^{-1} for the band at 6474A, corresponding to a moment of inertia of 2.78×10^{-40} gm. cm^2 or 2.80×10^{-40} gm. cm^2, respectively, about an axis perpendicular to the axis of symmetry. It would be very interesting to observe whether the other moment of inertia (about the symmetry axis) is not appreciably changed by the oscillation, as seems not improbable, but the accuracy of measurement scarcely suffices for this. The probable value for this quantity is 3.49×10^{-40} gm. cm^2 if one assumes a flat pyramidal structure for the ammonia molecule.

A particularly striking feature of the two harmonic bands is the alternation of intensity in each series. There seems to be a great tendency for alternate lines to be weak or to fall out altogether, and an alternation is also observed for corresponding lines through successive series. The irregularity of spacing in the P branch of the 3μ band suggests that the strong lines here do not all belong to the same series, and that greater resolution would disclose a similar condition in this case. Indeed this band seems quite similar to the harmonic at 6474A except that certain series which in the former are quite weak have in the latter become of intensity comparable with the strongest series.

For purposes of clarity the five series of the two harmonic bands have been represented in Figure 2 by means of a scheme similar to that which is frequently used in representing electronic bands. The diagonal lines sloping

to the left indicate the transitions giving rise to the P branches, and those sloping to the right to the R branches. J' and J'' are the probable values of the quantum number associated with the larger spacing of the band structure, in the normal and excited states respectively. The absolute values of the other quantum number τ for the several series are somewhat in doubt. The thickness of the diagonal lines represents roughly the intensity of the observed transitions, and as in Figure 1, broken lines indicate doubtful cases. At the bottom of the figure are shown the kinds of transitions which are especially characteristic of the two bands.

In the case of the band N, 0→4 the results indicate that the rotational levels are alternately of two kinds in both lower and upper states, one of these kinds being considerably the more probable. For the band N, 0→5 the

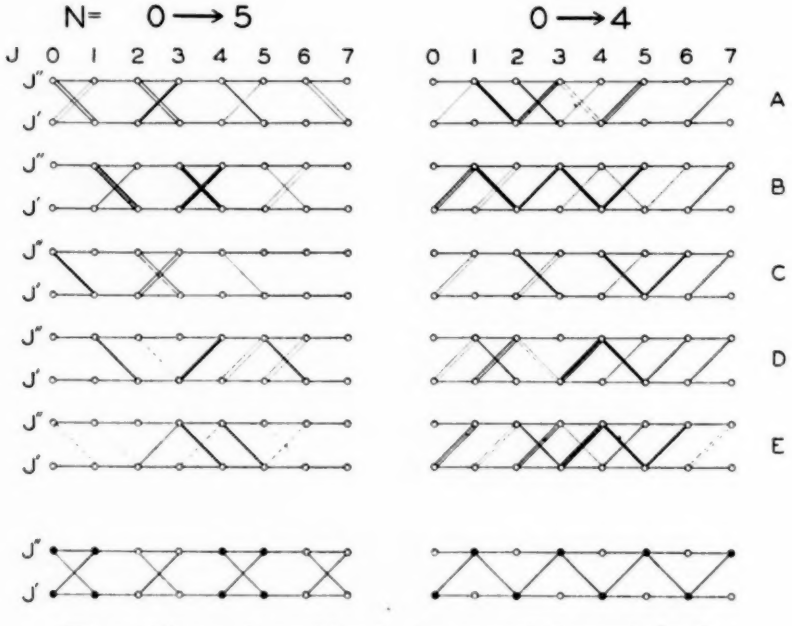

Fig. 2. Scheme of transitions in the ammonia harmonic bands.

situation seems to be quite different and the explanation is not obvious. In neither case is the condition quite what would seem to be predicted by the considerations of Hund.[2]

In this connection it is not out of place to make some remarks on certain other ammonia bands. At 10μ there is an absorption region which is produced by another type of molecular vibration. This band has been investigated by Barker,[5] who finds a double band of apparently simple structure. According to Barker's analysis this band comprises two component bands, each of which consists of a Q branch and simple P and R branches corresponding to the transitions $\Delta j = \pm 1$, $\Delta\tau = 0$. There is no appreciable convergence of the lines, and one component has a spacing of 20.2 cm,$^{-1}$ the other of 18.7 cm^{-1}. This would mean that the band is produced by two kinds of ammonia mole-

cule whose moments of inertia are the same in the upper and lower states but appreciably different from that of the lower state involved in the bands at 3μ etc. In other words these bands do not have a common lower level.

It seems to the writer, however, that the absorption curve may equally well be interpreted in a slightly different way, but one which is much more satisfactory when one considers its connection with the other data. The following analysis of the 10μ band is accordingly suggested.

TABLE II. *The ammonia band at 10μ. (from the data of Barker[5]).*

Band at 10.7μ or 933 cm^{-1}					Band at 10.3μ or 966 cm^{-1}			
ν_R	$\Delta\nu$	ν_P	$\Delta\nu$	Initial j	ν_R	$\Delta\nu$	ν_P	$\Delta\nu$
				14	1250	19		
				13	1231	18	711	18
				12	1213	15	729	21
		726	20	11	1198	19	750	20
1158	18	746	16	10	1179	18	770	19
1140	21	762	19	9	1161	18	789	19
1119	20	781	18	8	1143	18	808	20
1099	22	799	18	7	1125	19	828	21
1077	21	817	22	6	1106	19	849	19
1056	20	839	17	5	1087	18	868	21
1036	21	856	18	4	1069	20	889	20
1015	20	874	21	3	1049	20	909	19
995	—	895	16	2	1029	20	928	21
—	—	911	22	1	1009	—	949	17
955	22			0	—	—		
Mean $\Delta\nu = 19.6$ cm^{-1}					Mean $\Delta\nu = 19.3$ cm^{-1}			
Weighted mean $\Delta\nu = 19.83$ cm^{-1}					Weighted mean $\Delta\nu = 19.66$ cm^{-1}			

There is only one region of the absorption curve which does not fit this analysis as well as that given by Barker, and that is the weak maximum at 981 cm,$^{-1}$ which should include two maxima at about 975 cm^{-1} and 987cm^{-1}. It seems, however, that a more complete resolution of this region is necessary to decide definitely which interpretation is the correct one.

In the interpretation here suggested, the band at 933 cm^{-1} converges slightly in the P branch, which indicates a decrease of moment of inertia perpendicular to the symmetry axis, in the activated state. This is not surprising if one considers the type of vibration probably responsible for this band. The three hydrogen atoms are presumed to separate at the same time as the nitrogen atom is approaching their plane. The oscillation should be considerably nonharmonic with a tendency for the nitrogen atom to linger near the plane of the hydrogen atoms, causing a decrease of average moment of inertia as the amplitude of vibration increases.

The suggested interpretation of this band gives within experimental error the same moment of inertia for the normal state as that obtained from the other data.

In a study of the pure rotation spectrum of ammonia Badger and Cartwright[6] found an apparent convergence of the lines toward shorter wave-

[6] Badger and Cartwright, Phys. Rev. **33**, 692 (1929).

lengths. This spectrum consists of lines produced when j increases by unity, τ remaining constant. If this convergence is not real the molecular moment of inertia calculated from the lines of shorter wave-length, which were those most accurately measured, is the same as that calculated from the vibration rotation bands. But if the interpretation given for the doubling of these bands is the correct one, one should expect that the pure rotation lines are all double with components of perhaps unequal intensity. In this case it could appear that the unresolved lines were somewhat unequally spaced. A similar effect would not be observed, of course, in the case of the Raman spectrum.

At this point the author wishes to express his thanks to Professor J. Anderson of the Mount Wilson Solar Observatory of the Carnegie Institution for the loan of the ten-foot grating which made the investigation possible; and to Dr. Edison Pettit of the same institution for the microphotometer measurements.

EVIDENCE FOR QUANTIZATION FROM THE ELECTRIC POLARIZATION OF ACETIC ACID VAPOR

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(Received March 24, 1930)

Abstract

The dielectric constant of acetic acid vapor was measured at various pressures and temperatures. The results indicate a departure from Debye's theory which suggests an internal transition, with respect to temperature variation, from one type of single molecule to another. Near saturation there was detected a small amount of association of a kind increasing the molecular polarization. The anomaly is discussed from the point of view of the new quantum mechanics and it is suggested as an explanation that the effect is due to a transition from one state to a higher state of vibration associated with the OH group. The data are interpreted in terms of the proposed extension of Van Vleck's theory given in the following note. The Raman frequencies given by Dadieu and Kohlrausch indicate that the fundamental vibration frequency due to the OH group is of such a value as to produce transitions of quantum state in precisely the observed region of temperature. This is in agreement with the proposed theory, particularly since molecular polarization measurements in general indicate that the OH group always has associated with it a large electric moment.

The electric moment of the acetic acid molecule cannot be calculated accurately but the data indicate roughly a transition from 1.4×10^{-18} in the ground state to an average value greater than 1.7×10^{-18} c.g.s. e.s.u. in the upper states.

A discussion is given of the anomalous behavior of other physical properties of the vapor, regarding it as a statistical distribution of molecules, surrounded by different force fields associated with the change in electric moment. The possibility of attributing previously observed discrepancies between refractivities and the optical parts of the dielectric polarization to the above mentioned type of quantization is suggested.

IN THE measurement of the dielectric constant of vapors there have occurred occasional apparent deviations[1] from Debye's theory. These deviations are detected by a departure from linearity of the curve obtained by plotting the product of the molecular polarization and the absolute temperature against the absolute temperature itself. They occur always near the saturation point of the vapor, i.e., at low temperatures or high pressures. For this reason they have been attributed to association or adsorption on the condenser material. An associated molecule would give an increased contribution to the "optical" term of Debye's equation and a change in the "orientational" term corresponding to either an increased or a decreased electric moment.[2] The existence of association is to be detected by studying

[1] M. Jona, Phys. Zeits. **20,** 14 (1919); C. T. Zahn, Phys. Rev. **27,** 329 (1926); K. Wolf, Phys. Zeits. **27,** 588 (1926); K. Wolf, Ann. d. Physik. **83,** 884 (1927); F. Maske, Phys. Zeits. **28,** 533 (1927); J. B. Miles, Jr. Phys. Rev. **34,** 964 (1929).

[2] L. Ebert, Zeits. f. Physik. Chem. **113,** 1 (1924).

the variation of the polarization with pressure. Absorption could be detected in the same manner, but there is sometimes introduced a complication due to accompanying conductivity between the condenser plates. An anomaly of the latter type was observed by the author[3] in the case of water vapor at room temperature. The effect seemed to set in sharply at about one-third the saturation pressure. This adsorption was explained qualitatively by the attraction of the dipole molecule for its image in the adsorbing surface. As the molecule approaches the surface its potential energy is lowered until it touches the surface. The ratio of the pressure at the surface to that far from the surface is obtained by the Boltzmann distribution law. When the pressure in the body of the vapor reaches a certain value, that on the surface reaches saturation and adsorption follows. Originally it was thought that the observed effect was due to the direct dielectric effect of the layer of water on the condenser plates. This required about 200 layers of water. Later experiments were made by K. Wolf on this effect, and it was shown that there is considerable conductivity between the plates of the condenser. The author has also made measurements of this conductivity which show that the observed apparent increase in dielectric polarization may be largely due to the indirect effect of conductivity across the thin layer of water adsorbed on the quartz insulators used. It is impossible to say how much of the effect is due to each of the three causes, association, adsorption layer on the plates, and conductivity across the insulators. Fraser[4] has shown by measurements of the polarization of light reflected from the adsorbing surface of glass that about 5 layers of water are present at saturation. Therefore in the case of water vapor the effect must be almost entirely due to conductivity and possibly association. Only in case there is no observable conductivity can one be sure that a variation in molecular polarization with pressure is due to association (or chemical reaction).

All the above effects can usually be eliminated by working at pressures considerably below saturation, when one is interested in the polarization of single molecules.[5] In cases where there is no appreciable leakage in the condenser the anomalies can be used to obtain information concerning the forces causing association.[6] On account of the general anomalous behavior of the physical properties of acetic acid vapor it was thought that measurements of its dielectric constant might prove of interest, particularly since it is known definitely to associate in the gaseous state. By making pressure runs at each temperature and using only the linear, or low pressure parts, the polarization corresponding to the single molecules can be obtained. The Debye line obtained from these data should enable one to calculate the electric moment of the molecule and thus to obtain an idea of the magnitude of the moment characteristic of the carboxyl group. The upper or high pressure parts of the curves should give an idea of the nature of the association.

[3] C. T. Zahn, Phys. Rev. **27,** 329 (1926).
[4] J. H. Fraser, Phys. Rev. **33,** 97 (1929).
[5] c.f. C.T. Zahn, Phys. Rev. **35,** 848 (1930)
[6] P. Debye, "Polar Molecules," p. 41.

Experimental Results

The experiments here described were made by the same method used by the author in a series of previous investigations.[7] Pressure curves were obtained at eleven different temperatures in the range 20–220° C. In Fig. 1 are shown two typical pressure curves, one for a high temperature, and the other for a low temperature where the gas was nearer saturation. The high temperature curve shows no departure from linearity and therefore no as-

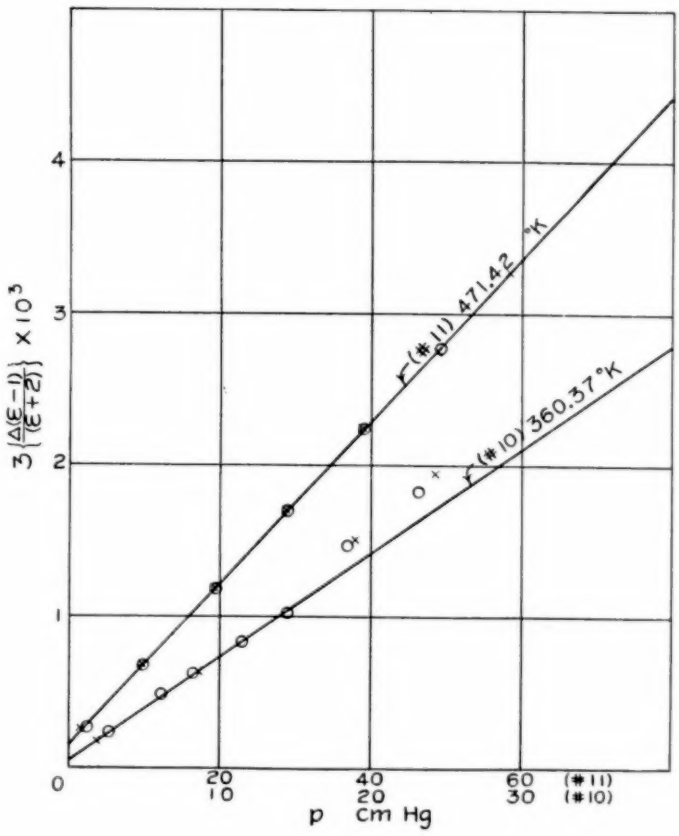

Fig. 1.

sociation. The low temperature curve has a linear portion at the lower pressures and an anomalous increase of the polarization for the higher pressure. near saturation. Leakage tests showed no appreciable conductivity. Therefore there is association of such a nature that the electric moment is increased.

A more interesting feature of the results is seen when an attempt is made to plot a Debye line. In Table I are given the data taken from the lower portions of the pressure curves where the effect of association is negligible. For economy in space the individual pressure data are not included. In

[7] C. T. Zahn, Phys. Rev. **24,** 400 (1924), C. T. Zahn, Phys. Rev. **35,** 848 (1930).

column III is given the limiting slope of the pressure curve in the lower part for pressures expressed in atmospheres. This gives the value of $(\epsilon-1)\,10^6$ corresponding to an atmosphere of single molecules. Column IV gives values of $3(\epsilon-1/\epsilon+2)\,(1/p_{at})$; and column V, values of $3(\epsilon-1/\epsilon+2)\,v\cdot 10^6$ where

TABLE I.

No.	T°K	$\frac{\epsilon-1}{p_{at.}}\cdot 10^6$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{10^6}{p_{at.}}$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right)v\cdot 10^6$	$3\left(\frac{\epsilon-1}{\epsilon+2}\right)vT$	P
1	410.84	4767	4760	7165	2.94_0	53.5
2	491.44	3742	3737	6724	3.30_4	50.2
3	357.78	5246	5235	6860	2.45_0	51.2
4	341.13	5461	5452	6809	2.32_3	50.8
5	389.64	5044	5036	7184	2.79_9	53.7
6	320.85	5791	5782	6792	2.17_9	50.7
7	450.09	4340	4334	7142	3.21_4	53.3
8	297.51	6764	6756	7359	2.18_9	55.0
9	493.86	3728	3724	6733	3.32_5	50.3
10	360.37	5246	5235	6907	2.48_9	51.6
11	471.42	4068	4063	7013	3.30_6	52.3

v is calculated from the ideal gas law $v=T/273.13p_{at}$. The van der Waal correction would probably amount to about one percent. This correction was not made because of the lack of data. Column VI gives the ordinates for the Debye line:

$$3\left(\frac{\epsilon-1}{\epsilon+2}\right)vT = AT + B.$$

Column VII gives values of the molecular polarization P, i.e., the value of $(\epsilon-1/\epsilon+2)$ corresponding to a gram molecule of single acetic acid molecules.

In Fig. 2 are plotted the values of columns VI and VII of the table. According to Debye's theory the upper curve should be a straight line of slope A and intercept B. The lower curve should be of the form:

$$P::A + (B/T).$$

It is obvious that this is far from the case and that there is here represented a departure from Debye's theory which is due neither to association nor to conducting layers. Apart from the linearity of the pressure curves in their lower parts, if there were association, it would be practically absent at the higher tempertures and the upper portion of the curve of Fig. 2 would approach the supposed true Debye line. Then the anomalous *decrease* of $3(\epsilon-1/\epsilon+2)vT$ for the lower temperatures would have to be attributed to association corresponding to *reduced* electric moment. On the other hand the pressure curves near saturation indicate that association occurs in such a way as to *increase* the electric moment of the molecule. Therefore an explanation of the departure from the Debye line based on the assumption of association leads to a contradiction.

The values for the lowest temperature, given in the table and shown in Fig. 2, were obtained under very difficult experimental conditions because of

the low vapor pressure, and are therefore subject to a much greater probable error. Association may not be completely eliminated. The slight rise in the upper curve is probably not correct, but the rise in the lower curve is probably only a little too great but definitely existing.

During the investigation it was thought that the observed anomalies could be due to an indirect effect of a small amount of water in the acid specimen. In order to test this supposition an especially pure specimen, of

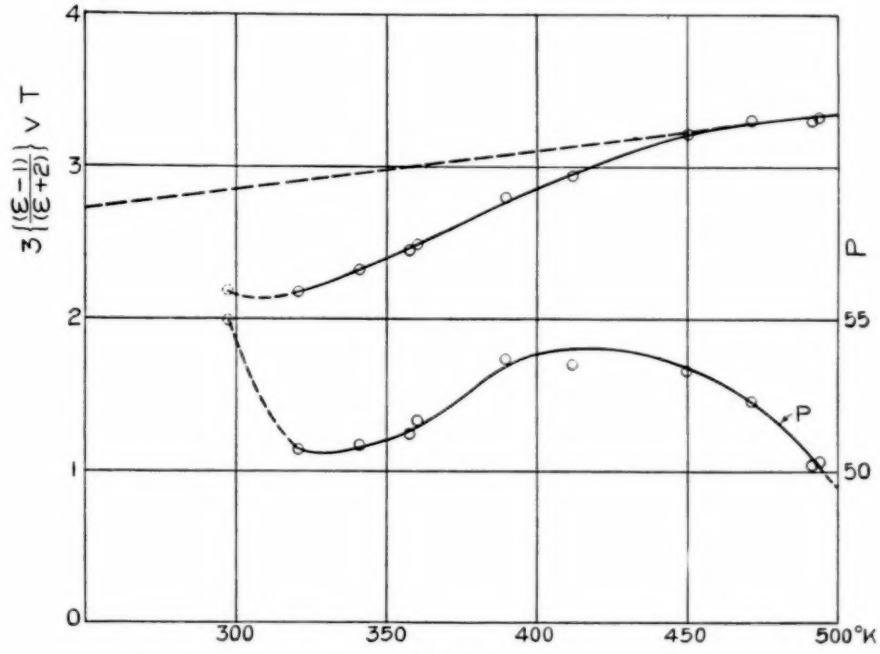

Fig. 2.

fusion point 16.6° C, was prepared and measurements were repeated at extreme temperatures. No appreciable difference was observed between the two specimens. In any case if the effect of water vapor is only its direct effect it would require a considerable amount to produce an appreciable change in the dielectric constant, since the two substances have nearly the same dielectric constant.

Evidence for Quantization

The curves in Fig. 2 indicate roughly a transition from one value of A and B in the Debye equation to another. Since the pressure curves are linear this must correspond to an internal change in the molecule. On the quantum theory such a change would be a change from one stationary state to another, or to a redistribution among several states, according to the Boltzmann theorem. Van Vleck[8] has given a general derivation of the Debye formula in the new quantum mechanics. The Debye formula is found

[8] J. H. Van Vleck, Phys. Rev. **29,** 729 (1927); Phys. Rev. **30,** 31 (1927).

to hold for temperatures such that $h\nu \ll kT$ where $h\nu$ is the energy spacing of the rotational levels or other low energy levels. This means that deviations due to rotational quantization are small when T is such that the above inequality holds. To a second approximation the effect of rotational quantization gives the formula:

$$3\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = A + \frac{B}{T} - \frac{C}{T^2}$$

Van Vleck has calculated the constant C in terms of the moments of inertia of the molecules and the components of the electric moment along the principal axes of inertia. When $T = h\nu/k$ the deviations are considerable and the above second approximation is not sufficient, of course. Debye[9] calls this latter temperature the "characteristic" temperature and finds that for HCl it is 14.7°K. At 0°C the correction due to rotational quantization is only about 2 percent, and it would be difficult to detect departures from the Debye formula unless measurements could be made near the characteristic temperature.

One can let each energy transition $h\nu$ define a temperature such that $h\nu = kT$. In this sense a transition in the region of $T = 400$°K could certainly not be attributed to rotational quantization since it would require a moment of inertia many times smaller than that of HCl. Van Vleck in his derivation of the Debye equation assumes that the electric moment of the molecule is invariant with respect to all quantum numbers producing low or medium frequency transitions. There are many substances which have vibrational energies in the region of measurable temperatures. If one admits the possibility of different "fixed" electric moment in different vibrational states the general behaviour of the curves in Fig. 2 can be explained as due to the statistical distribution in these states. In a note to follow Van Vleck's theory has been generalized to include such an assumption and Debye's formula is replaced by:

$$3\left(\frac{\epsilon - 1}{\epsilon + 2}\right) = A + \frac{\left[\Sigma_v B_v e^{-h\nu_v/kT}\right] / \left[\Sigma_v e^{-h\nu_v/kT}\right]}{T}.$$

This does not include the small correction due to rotational quantization. The B of Debye's equation is replaced by a statistically averaged B over all vibrational states. The same is true of the square of the electric moment since it is proportional to B.

In case the changes in the electric moment μ are due to a single type of vibration the various overtones ν_v will be spaced relatively far apart on the temperature scale, and in the region of temperature around a particular value of v the transition will be roughly as from one value of v to one other value. The higher energy states will exist in only small amounts. The general shape of the distribution curve in the two states according to the Boltzmann theorem is like the upper curve of Fig. 2. If the overtones be taken into

[9] P. Debye, "Polar Molecules," p. 150.

account the shape of the curve is only slightly changed in this region. Judging from such a distribution curve one would expect the transition frequency $h\nu_v$ to correspond to a temperature in the region from 420–450°K.

Relation to Raman Spectrum

Dadieu and Kohlrausch[10] have investigated the Raman spectrum of acetic acid in the liquid state and give lines of the following wave-numbers: 440 (0); 618 (1); 890 (4); 1430 ($\frac{1}{2}$); 1656 (1); and 2935 (4). Salant and Sandow[11] have shown that for HCl there is a small shift of the infra-red lines on passing from the liquid to the vapor states on account of the Lorentz force in the liquid. The frequency in the gaseous state was found to be of the order of 4 percent higher. This would not alter the following qualitative discussion. In the sense defined by $h\nu = kT$ these lines lie at temperatures: 307; 432; 622; 998; 1157; and 2050°K. Of these lines the only one definitely in the region of observed temperatures is the second at 432°K. This is a moderately strong line and is attributed by the above mentioned authors to the OH group of the molecule. This is in excellent agreement with what would be expected from the existing data on electric moments.[12] The OH group is known to have associated with it a large electric moment and therefore the Raman line associated with this group would be the most likely to produce changes in electric moment. The other lines in the Raman spectrum excepting the overtones of the OH line which are not sufficiently strong to appear, would probably cause only very small changes in electric moment. There may be also a small effect on the electric moment due to vibrations associated with the CO group, if the corresponding value of $h\nu$ is near the observed temperature region.

If the potential energy function associated with the vibration is unsymmetrical about the minimum point, the average nuclear separations may be quite different for the different quantum states. Accompanying this the electric moment might have quite different values, particularly in cases of weak bonds such as exist in large organic molecules. On the other hand it is just here that one would expect interaction between rotation and vibration or centrifugal expansion; and that the sum rules, discussed by Van Vleck in connection with the high frequency or optical part of the susceptibility, might be invalidated. It does not seem impossible that such disturbing effects might be small even if the electric moment is altered by the vibration. As another possibility, in a complicated organic molecule there might be more than one minimum value of the potential energy of vibration with fairly strong binding forces around each one of them. For example, in the case of the ammonia molecule, the potential energy of the nitrogen nucleus along the axis of the molecule is probably symmetrical, or nearly symmetrical, with respect to the plane of the hydrogen triangle and there exist two minima

[10] A. Dadieu and K. W. F. Kohlrausch, Monatsch. f. Chem. **52,** 220 (1929).
[11] E. O. Salant and A. Sandow, Phys. Rev. **35,** 214 (1930).
[12] H. A. Stuart, Phys. Zeits. **31,** 80 (1930).

on opposite sides of the triangle. In an organic molecule such a bond might be unsymmetrical and hence give rise to two distinct energy levels.

In connection with the above mentioned high frequency part of the dielectric susceptibility there are in progress in this laboratory observations of the refractivity of acetic acid vapor under the same conditions of pressure and temperature as the present observations. These observations may indicate whether any of the temperature variation is due to the failure of the sum rules which are called upon to prove the invariance of the high frequency term with temperature. They should also be of interest in connection with the association of the vapor near saturation. An observed variation with temperature could also be due to a variation in refractivity from one vibration state to another.

Electric Moment

On account of the inability to resolve completely the effects of the different states and of the lack of accurate knowledge of the Raman frequency for the vapor, it is impossible to obtain from the present observations an *accurate* knowledge of the electric moment in either state. Using a value of the refractivity obtained from the liquid one can calculate roughly the effective electric moment at the various temperatures. This is, of course, the root mean square electric moment. The calculation indicates that the average moment varies from 1.4 to 1.7×10^{-18} c.g.s. e.s.u. The lower value is probably not far from the value corresponding to the ground state. At the highest temperature there are still present a considerable number of the molecules in the ground state, which would necessitate a moment still greater than 1.7×10^{-18} for the upper state.

C. P. Smyth has recently made measurements[13] of the molecular polariza- of acetic acid solutions in benzene and in ether from 0 to 30°C. The values for the solution in benzene are in general abnormal. A calculation using the refractivity of acetic acid as above indicates an average moment of 0.7×10^{-18}. This may be due to a special type of association in the liquid state. For the solution in ether the behavior is normal and there is probably very little association as indicated by partition coefficient measurements. The value of the moment calculated by Smyth for this solution is 1.40×10^{-18}. At temperatures from 0 to 30°C all the molecules are probably in the ground state of vibration, judging from the curve of Fig. 2. The lower limit previously calculated from this curve, 1.4, is in good agreement with Smyth's value.

Physical Properties

In addition to the anomalous behavior here described acetic acid has long been known to behave anomalously with respect to van der Waal's equation. The value of $(RT_kd_k)/(Mp_k)$, which for most vapors is around 3.88, is abnormally high for acetic acid vapor, 4.99. Also Nasini[14] has recently measured

[13] To be published in the Jour. Amer. Chem. Soc.

[14] A. G. Nasini, Phil. Mag. **52**, 596 (1929).

the viscosity of acetic acid vapor at pressures of the order of 5 mm Hg and at temperatures from 90 to 250°C. At such low pressures there is no appreciable association, yet the temperature-viscosity curve shows at lower temperatures an opposite shape to those of other non-associated compounds.

If the interpretation of the behavior of acetic acid here suggested is correct it seems that the above mentioned deviations could be explained by the fact that such a vapor must be considered as a mixture of molecules surrounded by different force fields and distributed statistically. Any physical property depending on these force fields, such as van der Waal forces, mean free path, mobility, viscosity, etc., would be expected to behave abnormally with respect to temperature variation.

This effect of the variation of electric moment with vibrational state may be of some small importance even in molecules such as HCl where Debye's theory is apparently obeyed. If the vibration frequencies are not near the observed temperature region and if the moment is slightly different for different quanta of vibration, there may still be a first order linear correction to be applied. This would not alter the linearity of the Debye line but would give a slightly erroneous electric moment, and an erroneous value of the "optical" part, A, of the susceptibility. In a number of cases[15] where the electric moment is large there have been discrepancies between the value of A and the refractivity. A is usually higher than the refractivity. In the case of the halogen hydrides the discrepancy is larger the larger the electric moment. These discrepancies have been discussed by various authors, notably Van Vleck,[16] without obtaining a satisfactory explanation. For the case of HCl Van Vleck has made calculations to show that the effect of the vibrational spectrum on the dielectric constant is negligibly small. It should be noted in this connection that he has assumed an electric moment fixed with respect to the vibrational quantum number. In the case of CO_2 Fuchs[17] has shown that the atomic vibration frequencies are necessary for the extrapolation of the refractivity to infinite wave-length, and that the value so extrapolated agrees well with the polarization obtained from electrical measurements. The discrepancies then may be due either to an error in the refractivity by the failure to include the atomic vibration frequencies when they are important, or to an erroneous value of A caused by vibrational quantization, when there is a variable electric moment, and possibly to a much smaller extent by the rotational quantization. There may also be a temperature effect on the high frequency part A caused by the failure of the sum rules for molecules with loose bonds; and the value of A obtained from dielectric constant data on the assumption that it is constant would be in error.

[15] C. T. Zahn, Phys. Rev. **24,** 400 (1924).
[16] J. H. Van Vleck, Phys. Rev. **30,** 44–46 (1927).
[17] O. Fuchs, Zeits. f. Physik **46,** 519 (1928).

AN EXTENSION OF VAN VLECK'S THEORY OF DIELECTRIC POLARIZATION

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(Received March 24, 1930)

Abstract

The experimental data in the preceding paper show a departure from the Debye equation:

$$\left\{\frac{\epsilon-1}{\epsilon+2}\right\}\frac{1}{d}=A+\frac{B}{T}$$

suggesting an effect of vibrational quantization where the electric moment depends on the vibrational quantum number. Van Vleck assumed the electric moment fixed for all states of low energy and thus did not admit the above possibility. In the following note it is shown that Van Vleck's theory can easily be extended to include the effect of such vibrational quantization which may occur in the region of observed temperatures. Debye's equation no longer holds in its simple form. In a sense it can be regarded to hold if the vapor be considered as a mixture of molecules statistically distributed in the vibration states.

THE following is simply an extension of Van Vleck's[1] theory of dielectric polarization and differs from his treatment only in the degree of restriction of the assumptions. He considers all the quantum numbers effective on the molecule to be divided into three classes, n, j, and m. The index n includes all quantum numbers whose effect is such that $h\nu \gg kT$; the index j, such that $h\nu \ll kT$, excluding the axial quantum number; and m, the axial quantum number for which also $h\nu \ll kT$. n may include electronic and vibrational quantum numbers; j, inner, rotational, and spin; and m, axial. In many vapors there are vibrational states for which $h\nu \sim kT$. As Van Vleck states, under his assumption of invariant "fixed" moment, these states, which correspond to linear oscillators, would cause no temperature variation; but they will be important under the present assumptions. For this reason there will be included an index v for the cases where $h\nu \sim kT$. This will be considered to correspond to some of the vibrational states.

Considering, as did Van Vleck, the electric moment matrix of typical element,

$$M_z(nvjm;\ n'v'j'm')e^{2\pi i\nu(nvjm;n'v'j'm')t}$$

the dielectric susceptibility can be written:

$$\chi=\frac{N}{F}\frac{\Sigma_{vjm}M_z^{(F)}(nvjm;\ nvjm)e^{-W^{(F)}(nvjm)/kT}}{\Sigma_{vjm}e^{-W^{(F)}(nvjm)/kT}} \tag{1}$$

where all the molecules are assumed to be in the ground state indicated by n. The perturbation theory gives, to the first power in F:

[1] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927).

$$M_z^{(F)}(nvjm; nvjm) = M_z(nvjm; nvjm) - \frac{2F}{h}\Sigma_{n'v'j'm'}\frac{M_z(nvjm; n'v'j'm')^2}{\nu(nvjm; n'v'j'm')} \quad (2)$$

and

$$W^{(F)}(nvjm) = W(nvjm) - FM_z(nvjm; nvjm). \quad (3)$$

Substituting (2) and (3) in (1) gives:

$$\begin{cases} \chi = \dfrac{N}{F}\dfrac{\Sigma_{vjm}M_z(nvjm; nvjm)e^{-W(nvjm)/kT}}{\Sigma_{vjm}e^{-W^{(F)}(nvjm)/kT}} & (a) \\ \quad + \dfrac{B}{kT}\Sigma_{vjm}\mid M_z(nvjm; nvjm)\mid^2 e^{-W(nvjm)/kT} & (b)\ (4) \\ \quad - \dfrac{2B}{h}\Sigma_{vjm;n'v'j'm'}\dfrac{\mid M_z(nvjm; n'v'j'm')\mid^2 e^{-W(nvjm)/kT}}{\nu(nvjm; n'v'j'm')} & (c) \end{cases}$$

where:

$$B \equiv N/\Sigma_{vjm}e^{-W(nvjm)/kT}. \quad (5)$$

4(a) vanishes because there is no residual electrifications for the field intensity $F=0$. (4) can now be written:

$$\begin{cases} \chi = \dfrac{B}{kT}\Sigma_{vjm}\mid \mu_z(vjm; vjm)\mid^2 e^{-W(nvjm)/kT} & (a) \\ \quad - \dfrac{2B}{h}\Sigma'_{vjm;vj'm'}\dfrac{\mid \mu_z(vjm; vj'm')\mid^2}{\nu(nvjm; nvj'm')}e^{-W(nvjm)/kT} & (b)\ (6) \\ \quad - \dfrac{2B}{h}\Sigma_{vjm;n'v'j'm'(n',v'\neq n,v)}\dfrac{\mid M_z(nvjm; n'v'j'm')\mid^2}{\nu(nvjm; n'v'j'm')}e^{-W(nvjm)/kT} & (c) \end{cases}$$

where for the low frequency elements $M_z(nvjm; nvj'm') \equiv \mu_z(vjm; vj'm')$ for separate treatment. For a fixed value of v 6(b) can be grouped in pairs and by approximate expansion put into the same form as 6(a) and included under a general summation (c.f. Van Vleck). Then (6) becomes:

$$\begin{cases} \chi = \dfrac{B}{kT}\Sigma_v\Sigma_{jm;j'm'}\mid \mu_z(vjm; vj'm')\mid^2 e^{-W(nvj)/kT} & (a) \\ \quad - \dfrac{2B}{h}\Sigma_v\Sigma_{jm;n'v'j'm'(n',v'\neq n,v)}\dfrac{\mid M_z(nvjm; n'v'j'm')\mid^2}{\nu(nvjm; n'v'j'm')}e^{-W(nvjm)/kT} & (b) \end{cases} \quad (7)$$

where $W(nvjm) \equiv W(nvj)$ since the m separations are small.

On account of the high degree of spectroscopic stability $\sum_{mm'}\mid \mu_z(vjm; vj'm')\mid^2$ is invariant of the direction of space quantization and can be written $\frac{1}{3}\sum_{mm'}\mid \mu(vjm; vj'm')\mid^2$. If the energy spacings due to j and m are small compared to those associated with v and n then for 7(b) $\nu(nvjm; n'v'j'm') \rightarrow \nu(nv; n'v')$ and $W(nvjm) \rightarrow W_v$. This latter requirement may not always be satisfied in actual cases, particularly with reference to the index v, but will

probably be met in most cases. Also $\sum_{jm} |\mu(vjm; vj'm')|^2$ is the diagonal element $\mu^2(vjm)$ of the μ_v^2 matrix. This fixed moment is assumed independent of (jm), but not of v as in Van Vleck's treatment.

All these facts together with (7) and (5) give:

$$\chi = \frac{\Sigma_v N\{\alpha_v + (\mu_v^2/3kT)\}e^{-W_v/kT}}{\Sigma_v e^{-W_v/kT}} \tag{8}$$

where

$$\alpha_v \equiv -\frac{2}{3h}\Sigma_{jm;n'v'j'm'(n',v'\neq n,v)} \frac{|M_z(nvjm; n'v'j'm')|^2}{\nu(nv; n'v')}$$

represents the high frequency terms. As Van Vleck has shown α_v will be independent of temperature if the sum rules for absorption are applicable. These rules, according to Dirac, should be easily extended to any molecules for which the internal coupling forces give rise to pure precessions and not to distortions such as centrifugal expansion. On the other hand it is in just such molecules where the binding is weak and the electric moment depends on the state of vibration that the effects of centrifugal expansion would be expected. Therefore it is possible that each α_v depends on the temperature to a small extent in case the sum rules break down. The high frequency term then is subject to three possible causes of small temperature variaton: redistribution amongst the α_v for different vibration states, a breaking down of the sum rules, and the effect of j quantization which was neglected in setting $W(nvjm) = W(nv)$ and $\nu(nvjm; n'v'j'm') = \nu(nv; n'v')$.

Further α_v is probably nearly independent of v for the following reasons. It has long been known that the law of additivity of atomic refractivities holds fairly well except in molecules with polar bonds. Therefore one would expect that α_v would not change very much in going from one vibration state to another if the accompanying changes in electric moment were only a small fraction of the total fixed moment. Still this effect might be much greater than that due to the breaking down of the sum rules or to the j quantization. If we do make the assumption that α_v is independent of v (8) becomes:

$$\chi = N\left\{\alpha + \frac{\Sigma_v(\mu_v^2/3kT)e^{-W_v/kT}}{\Sigma_v e^{-W_v/kT}} \cdot \frac{1}{T}\right\} \tag{9}$$

or:

$$\chi = A + \frac{\Sigma_v B_v e^{-W_v/kT}}{\Sigma_v e^{-W_v/kT}} \cdot \frac{1}{T} \tag{10}$$

where the constants A and B_v correspond to those in Debye's equation. In these equations the effect of rotational quantization is neglected. This has been discussed by Van Vleck, Debye, and others for the low frequency term. As a first approximation there is introduced a term $(-C/T^2)$ in the expression for χ.

In conclusion the author wishes to express his indebtedness to Dr. G. Breit for the opportunity to discuss with him several aspects of this problem.

ON A NEW PHOTOELECTRIC EFFECT IN ALKALI CELLS

By Erich Marx
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(Received March 13, 1930)

Abstract

If two monochromatic beams fall simultaneously on an alkali electrode, a new photoelectric effect is shown as follows: If the intensity of the high frequency light ν_1 is sufficient to establish the limiting potential corresponding to the Einstein law, the presence of any component of lower frequency ν_2 diminishes the potential according to the following equation

$$R = c\ (n_2/n_1)\cdot(\nu_1/\nu_2)(\nu_1-\nu_2)h/e$$

where R is the potential decrease and n_2/n_1 the ratio of the electronic emission of the two components, measured by the test cell itself. A tentative explanation of the phenomenon is advanced.

I.

IN A preliminary note to Die Naturwissenschaften[1] I have described a new photoelectric effect in alkali cells. The existence of this effect was denied by Olpin.[2] In the present article we present the essential experiments on which the original note was based.

The effect is as follows. If light of frequency ν falls on a potassium surface the limiting potential V is given by Einstein's law $h(\nu-\nu_0)=\epsilon\cdot V$, where ν_0 is the long wave limit and h the Planck constant; $h\nu_0$ is equal to the contact potential of the potassium in the cell. If the insulation of the electrodes is sufficient, and the light intense enough, the limiting potential should depend only on the shortest radiadion which is contained in the incident beam.

Our experiments show conclusively that if white light falls on a highly evacuated potassium cell, which is so constructed that the anode is shielded from all light, direct as well as reflected, a limiting potential is reached. If now a blue glass filter is put in the path of the incident light, the limiting potential is increased. Since the filter cannot possibly add light of higher frequency, it is obvious that we are dealing with a new phenomenon. The limiting potential is consequently diminished by the presence of the long wave radiation.

At the Breslau meeting of the Deutschen Physikalischen Gesellschaft in January of this year, I demonstrated this effect by two different experiments. In the first experiment light passing through a small diaphragm was permitted to fall on the photoelectric cell, until a constant potential was shown by the string electrometer connected to the cell. A neutral gray

[1] Marx, Die Naturwissenschaften **17**, 806–807 (1929).
[2] A. R. Olpin, Phys. Rev. **35**, 112 (1930).

filter was then interposed. No change was shown by the electrometer demonstrating that the conditions of light intensity and insulation were fulfilled. When I replaced the gray filter by a blue filter the electrometer showed an increased potential, although the intensity of the incident light was diminished to 1/5 by the blue filter. In the second experiment the incident

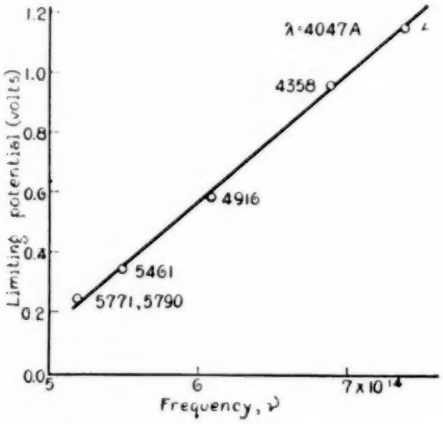

Fig. 1. Dependence of electrometer potential on the wave-length.

light was split into two beams. In the path of one beam an orange filter (Schott filter OG 2) was placed and in the path of the other a blue filter (BG 4) was placed. When the blue beam alone was permitted to fall on the cell, the electrometer showed a constant potential, but when the orange beam also was permitted to fall on the cell the electrometer potential decreased to a new constant value.

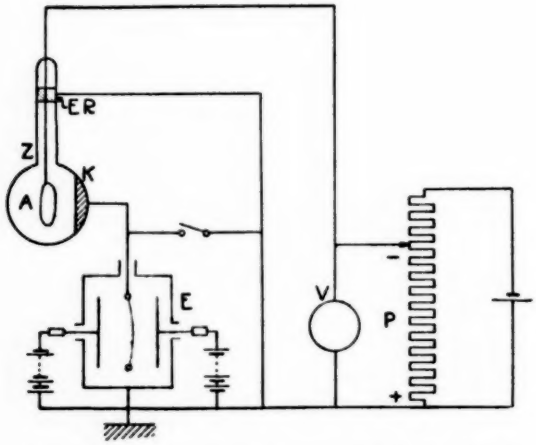

Fig. 2. Compensation device for measuring the limiting potential.

In my first experiment I demonstrated the effect by subtracting long wave-length light from the original beam; in the second experiment I demonstrated the same effect by adding orange light to the beam.

II. The effect shown by the above qualitative experiments has been investigated completely and quantitatively by A. H. Herbert Meyer and myself using a double monochromator in place of the glass filters. We found without exception that whenever the cell is illuminated simultaneously with a shorter and a longer wave-length beam, that the electrometer potential is less than if the cell is illuminated by a shorter wave-length beam alone.

We next investigated our photoelectric cell. Fig. 1 shows the dependence of electrometer potential on the wave-length. The linear dependence and the slope of the line are completely in agreement with the best experimental

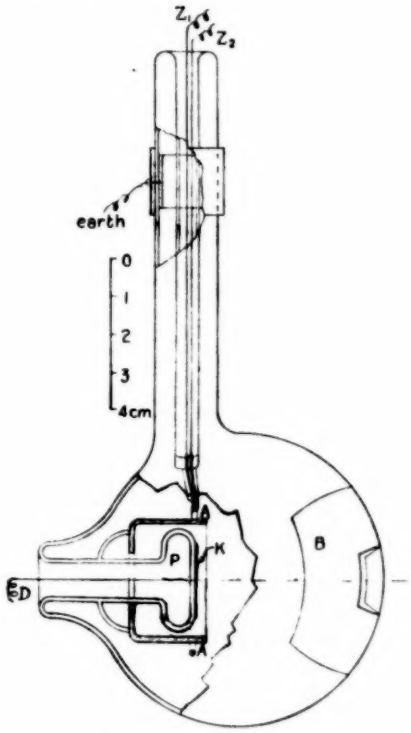

Fig. 3. Diagram of cell.

values of h and e. We used two different methods for these investigations both of which were different from the known pioneer method of Millikan. In the first method we measured the deflections of a string electrometer, in the second method, we used a compensation device, shown in Fig. 2. V is a precision voltmeter. The two methods were in complete agreement, but the compensation method has the advantage of introducing a guard ring. This compensation method is superior to the other mentioned with respect to accuracy and rapidity of measurement. The cell used for this purpose was of the kind sketched in Fig. 3. The tube was evacuated as well as could be done in the presence of potassium. The potassium layer

K was deposited on the platinized front of the glass mushroom P. The contact was established by the wire D. The anode AA formed an almost complete annular ring, with contacts by the lead wire Z_1Z_2. This arrangement permitted us to heat the anode. The shield G was made of black glass which protected the anode from all reflected and scattered light. The interior surface of the bulb was covered with a very thin potassium layer. B was a tin

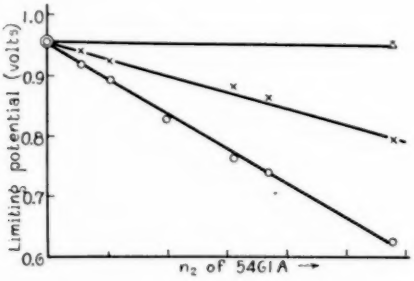

Fig. 4. Dependence of limiting potentical for three different intensities of 4358A when mixed with various intensities of 5461A.

foil covering on the outer surface, in which a rectangular opening was cut. It was electrically connected with the interior surface and the cathode K, all of which was kept at earth potential. The compensating potential was applied to the anode only. This form of cell gave the very satisfactory results of Fig. 1.

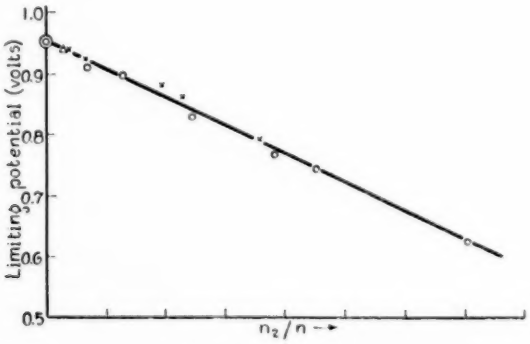

Fig. 5. Dependence of limiting potential upon the ratio of the intensity of the components.

Although it is not necessary to shield the anode in order to demonstrate the qualitative effect of light mixtures, it is necessary to do so if we wish to obtain quantitative results. The precautions which must be taken in order to obtain results of highest accuracy will be discussed by Mr. A. H. Herbert Meyer in his thesis, which will soon be published.

III. After obtaining the results plotted in Fig. 1 we then investigated the effect of light mixtures.

Fig. 4 shows the dependence of the limiting potential for three different intensities of the blue line 4358A, when mixed with various intensities of

the green line 5461A. By intensities we mean the amount of light which results in electronic emission. The three blue intensities were 139 erg/sec, 11.4 erg/sec and 5.8 erg/sec. It is to be noticed that when no green light was admitted, the electrometer showed exactly the same potential. When green light was admitted the limiting potential depends not only upon the intensity of the green line but also upon the intensity of the blue line. The

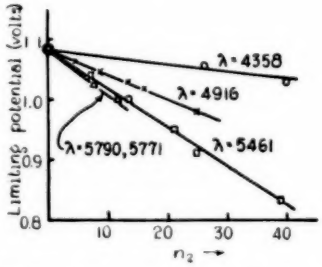

Fig. 6. Dependence of limiting potential of λ4047 when mixed with various intensities of different longer wave-lengths.

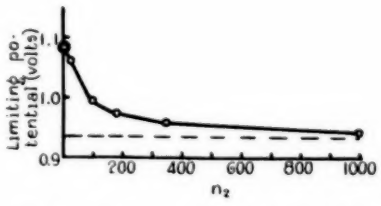

Fig. 7. Dependence of the limiting potential of λ4047 upon the intensity of λ4358 up up very high intensities.

dependence is linear. This can be more conveniently shown in Fig. 5 by plotting the potential against n_2/n_1 as is done for all data contained in Fig. 4.

IV. We next tried the effect of varying the frequencies of the long wave-length component, keeping the frequency and intensity of the high frequency component constant. For a high frequency component we chose the line 4047A, since this is the highest frequency in the mercury spectrum which glass transmits with sufficient intensity.

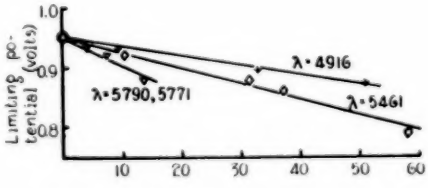

Fig. 8. Dependence of limiting potential of λ4351 when mixed with various intensities of different longer wave-lengths.

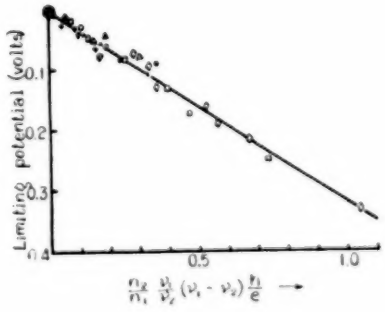

Fig. 9.

In Fig. 6 we have plotted the limiting potentials for this line when mixed with various intensities of the lines λλ4358, 4916, 5461 and 5790–5771A. It is evident that in all cases we get a linear dependence. The intensities were determined by a helium cell before and after measurement of the limiting potential in our test cell. This helium cell had already been compared with our test cell and a thermocouple at various frequencies.

If the intensity of the low frequency components is increased still more, keeping the intensity of the short wave component constant, a point is reached where the linear dependence ceases. The curve approaches asymptotically to the value it would have for the pure low frequency component (Fig. 7).

Fig. 8 is exactly the same as Fig. 6 except that in this case we used the line λ4358A for high frequency component in place of λ4047A.

V. As may be seen from the linear form of the curve of Fig. 9, all our observations can be fairly well represented by a straight line. The lowering of the limiting potential is therefore given by

$$R = \text{const.}\,\frac{n_2\nu_1}{n_1\nu_2}(\nu_1 - \nu_2)\frac{h}{e}$$

where n_2/n_1 is the ratio of the intensities of the components and ν_1 and ν_2 are the frequencies of the shorter and longer wave-length components, respectively.

VI. In the Einstein law the $h\nu_0$ term which represents the work of emission is independent of the frequency of the light which falls on the photoelectric substance for a given substance. We could therefore expect this work

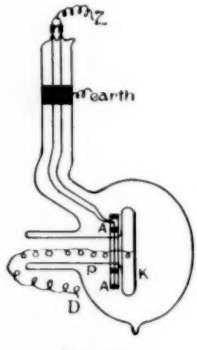

Fig. 10.

to be constant for light mixtures. The obvious explanation of the effect which we have observed would be that the anode is emitting electrons and therefore the equilibrium potential is lowered. This was the first point that we tested by constructing a cell, in shape of a dumbbell, in one side of which was the anode ring and in the other the potassium. The diameter of the anode was so large, that none of the light which passed through the connecting tube could fall on the anode. It was therefore completely shielded from both direct and reflected light. The possibility of explaining the observed effect by assuming an electron emission on the anode is very nearly excluded. In order to make absolutely certain of this point we constructed the cell shown in Fig. 10. In this cell the anode lies behind the cathode and is still further shielded from it by black glass which half incloses the anode. This cell gives exactly the same results as the cell which was used in this

investigation. Due, however, to the unfavorable form of the field in the cell it took too long actually to use this cell in the investigation. We have, however, tried such a cell in which potassium was replaced by sodium. This sodium cell behaves exactly like the potassium cell. This does not agree with the results in the letter mentioned above.

VII. The explanation of the determination of the limiting potential by light of long wave-length is the following. As a result of the general distribution of velocities, as given by Ramsauer, it follows that in the case of limiting potential there must be, even with monochromatic light, a distribution of space charge extending over the whole distance between anode and cathode. The magnitude of the space charge is determined by capacity and limiting potential. This gives all the conditions necessary and sufficient for the theory.

The integration of the Poisson equation gives the variation of the distribution of the space-charge as a function of the frequency. Now, if long-wave light is incident along with short-wave light, then the space charge resulting from the long-wave light (just as the charging of the illuminated electrode) can only be generated at cost of the electrons, set free by the short-wave light. Since each electron which is released returns to the illuminated electrode, the number of electrons produced by light of frequencies ν_1 and ν_2 is equal to the number n_1 and n_2 respectively which is present in the space between anode and cathode. The ratio n_1/n_2 of the electrons, produced per second from frequencies ν_1 and ν_2, determines therefore the proportion in which the electrons generated by these frequencies take part in the emission and are present in the space charge. If by illumination with short-wave light alone the limiting potential was attained, then this will sink, when the repressing of the electrons generated by short-wave light has advanced to such a degree, that the number of electrons released per second is no longer sufficient to charge up the illuminated electrode to the limiting potential. The limiting potential then approaches asymptotically the limiting potential of the long-wave light as in diagram 7.

The publication of the complete theory follows in the near future.

OSCILLATIONS IN THE GLOW DISCHARGE IN NEON

By Gerald W. Fox
Department of Physics, University of Michigan

(Received February 26, 1930)

Abstract

Radio-frequency oscillations consisting of one or two fundamentals together with a series of harmonics for each fundamental have been observed in large current glow discharges in neon. The observed frequencies lie in the range from approximately 1.5×10^4 to 2×10^5 cycles per second. The oscillations are very sensitive to pressure changes, their frequency increasing rapidly with decreasing gas pressure. The oscillation frequency also increases markedly with increasing current. The frequency is quite independent of resistance in series with the discharge.

The suggestion is made that the oscillations are due to the presence of a reversed electric field in the negative glow of the discharge.

Introduction

OSCILLATIONS in gaseous discharges have been observed for many years. As far back as 1876, Spottswoode[1] reported observing intermittant electric discharges in gas filled tubes. More recently the work of Whiddington,[2] Appleton,[3] Penning,[4] Webb and Pardue,[5] Tonks and Langmuir,[6] and others have brought this phenomenon to the fore, with the result that many new and interesting data have come to light. The present paper deals only with glow discharges in neon.

Apparatus and Method

The discharge tube is shown in Fig. 1. The over all length was approximately 50 cm, of which the central section was a quartz tube 22 cm long and 2 cm in diameter. The two Pyrex bulbs contained respectively the heavy copper anode, *P* and the barium-oxide coated cylindrical nickel cathode, *C*. The cathode was indirectly heated by radiation from a 20 mil tungsten spiral inside. A close fitting glass sleeve diminished gas diffusion to the back of the anode so that only the front was effective. Ground joints, deKhotinsky sealed, connected the central quartz section to the two end bulbs. These joints were water cooled. The tube voltage was supplied through series resistance by a 600 volt storage battery.

The usual arrangement of pressure gauges and pumping equipment made up the vacuum system. The discharge tube itself was at all times isolated

[1] Spottswoode, Proc. Roy. Soc. May 18 (1876).
[2] Whiddington, Engineering, **120**, 20 (1925)
[3] Appleton, Phil. Mag. **45**, 879 (1923).
[4] Penning, Phys. Zeits. **27**, 187 (1926).
[5] Webb and Pardue, Phys. Rev. **32**, 946 (1928).
[6] Tonks and Langmuir, Phys. Rev. **33**, 195 (1929).

from the pumping system by a liquid air immersed charcoal trap close to the anode bulb, and a second liquid air trap nearer the pumps. At no time throughout the period of the experiments did the discharge show the presence of mercury vapor.

The detection scheme was essentially the same as that used by Webb and Pardue.[5] A regenerative detector circuit and a one stage audio amplifier worked admirably. The current through the discharge tube flowed through a

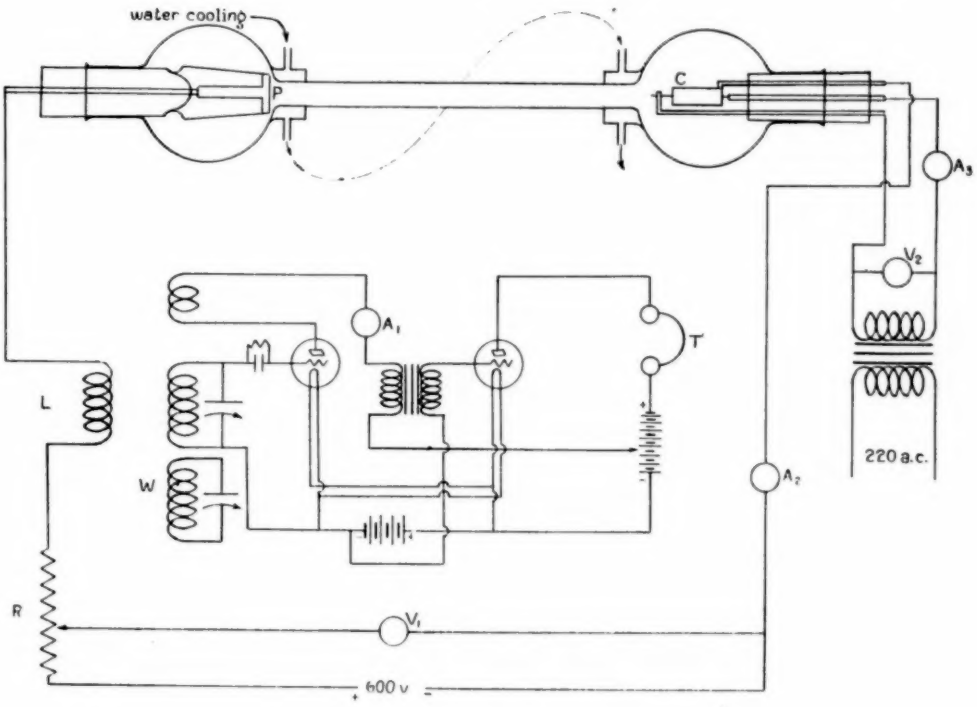

Fig. 1. Diagram of apparatus.

five turn coil of heavy wire which was very loosely coupled to the input of the detector tube. The frequency of the discharge was determined through the method of beats. On zero beat the frequency was measured by a loosely coupled wavemeter.

Results

1. *Frequencies present at a given pressure.*

Data taken in a large number of runs show that several frequencies were present in the discharge at the same time. These frequencies appear to be multiples of a fundamental frequency. The pick up circuit allowed complete covering of a wave-length range of 24000 meters to 100 meters. Throughout this range a large number of frequencies were found. Table I shows one typical run and Table II another. It will be noticed that these are for different tube currents and gas pressures.

TABLE I. *Observed frequencies in glow discharge in neon.* (Tube current 1 ampere, tube voltage 170 volts, Gas pressure 0.52 mm Hg).

Wave-length (meters)	Frequency (cycles/sec)	Order
19800	15151	1
9540	31446	2
6580	45592	3
3960	75757	5
2830	106007	7
2480	120968	8
1990	151753	10
1800	166666	11

TABLE II. *Observed frequencies in glow discharge in neon.* (Tube current 3 amperes, tube voltage 165 volts, gas pressure 1.8 mm Hg).

Wave-length (meters)	Frequency (cycles/sec)	Order
15460	19404	1
7700	38961	2
5150	58252	3
3900	76923	4
3080	97402	5
2580	116279	6
2200	136363	7
1930	155440	8

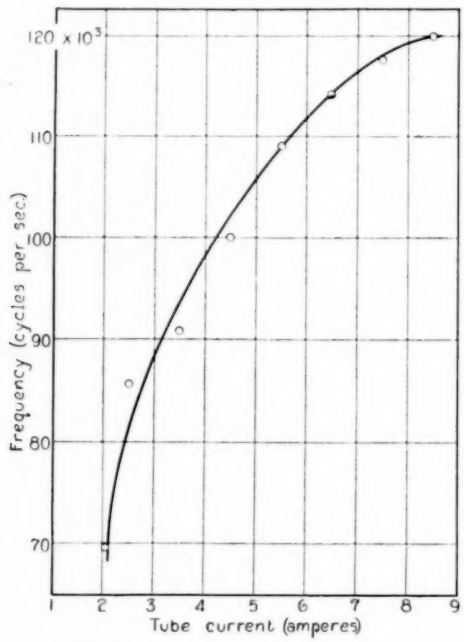

Fig. 2. Typical curve showing variation of oscillation frequency with tube current in neon.

2. *Variation of frequency with tube current.*

The curve shown in Fig. 2 is typical of the frequency variation with tube current. The frequency at first rose rapidly with the increase in current; then more slowly. However, it never reached a condition where it no longer changed with increase in current. At some current value there was always an abrupt change, the frequency stopping suddenly and some other fundamental appearing with its corresponding series of harmonics.

3. *Variation of frequency with pressure.*

The discharge frequency was extremely sensitive to pressure changes. Even the slight pressure fluctuations caused by raising or lowering the mercury in the McLeod gauge were enough to vary the beat note as heard in the

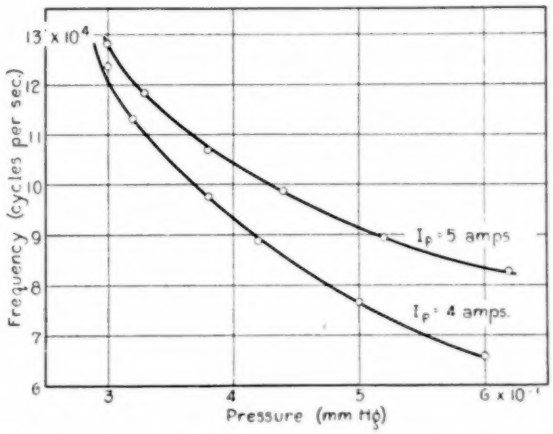

Fig. 3. Variation of oscillation frequency with gas pressure in neon.

telephone receivers as much as a thousand cycles. Fig. 3 shows typical frequency-pressure curves. The frequency rose very rapidly as the pressure was lowered to 0.2 mm of mercury. Below 0.2 mm it became increasingly difficult to maintain oscillations. Their regularity disappeared and, although even at 0.01 mm for some current values the discharge could be made to oscillate, conditions were very uncertain.

4. *Oscillations independent of series resistance.*

Table III shows that the oscillation frequency is not a function of the series resistance.

TABLE III. *Independence of oscillations of series resistance.* (Tube current = 3 amperes, pressure = 0.57 mm).

Total voltage	Tube voltage	Series resistance (ohms)	Frequency
500	175	108	88495
325	175	47	88235
230	175	18	87915
190	165	8	88626

These data were taken within a period of five minutes. The discharge was off only long enough to allow decreasing the total battery voltage.

Discussion

The oscillations here investigated exist only when the discharge is perfectly steady with a uniform positive column. They are entirely unaffected by any capacitance or inductance in parallel with the discharge. In Appleton's[3] work on ionic oscillations the inference is made that oscillations occur in sharply defined striae. In the work of Webb and Pardue[5] the oscillations do not exist so long as sharply defined striae are present but begin when diffusion between adjacent striae takes place and continue until a uniform glow fills the tube. In both the investigations mentioned the tube currents were small, of the order of a few hundred milliamperes at most, while in this investigation the tube currents varied from one ampere to as much as twenty amperes. Oscillations consisting of one or two fundamentals and numerous harmonics were present for any current in this range providing the pressure was not too low.

In their theory of plasma-ion oscillations Tonks and Langmuir[6] have developed an expression for the frequency of ionic oscillations. The limiting value is given by:

$$\nu = e^2\left(\frac{n}{\pi m}\right)^{1/2}. \tag{1}$$

Under the conditions of their experiments the limiting value for mercury vapor comes out to be about 1.5×10^6 cycles per second. According to their theory the plasma-ion type of oscillation is likely to go over into electric-sound waves, whose frequency may extend up to 6.5×10^5 per second. The frequencies observed in this investigation fall in this range. The variation of frequency with gas pressure is in general agreement with the curves of Webb and Pardue.[5]

It seems very certain that the type of oscillation herein described does not depend on series resistance. As shown in Table III there is a negligible frequency change for different values of series resistances. In fact the discharge has an entirely positive characteristic since it will run steadily with no series resistance at all, except the very small value due to lead wires from the storage batteries, provided the total voltage across the tube does not exceed by more than a few volts the usual drop across the tube (about 170 volts for this tube). The cathode temperature is not affected appreciably by positive ion bombardment but is wholly controlled by radiation from the heater coil.

Compton and Eckert[7] have shown that oscillations may exist in discharges of the low voltage arc type when there is a high resistance in series with the arc. As the voltage across the tube increases to the ionization potential of the gas, the arc strikes. The negative space charge surrounding the filament is at once neutralized by the positive gas ions. Bombardment of the filament in-

[7] Compton and Eckert, Phys. Rev. **24**, 97 (1924).

creases its temperature, thereby further increasing the emission and hence the arc current. But the resulting large $I\,R$ drop in the series resistance lowers the voltage across the tube. This constitutes one type of oscillation. The glow discharge is not greatly different from a low voltage arc except for the long positive column. One might expect, therefore, a similar explanation of the origin of the oscillations, but the evidence is against this.

At all times during the experiments, the interesting flashes described by Aston and Kikuchi[8] and Whiddington[2] were present. The suggestion is made that the ionic high frequency oscillations are modulated by these rather low frequency pulsations, since on zero beat a note of about 150 cycles was always

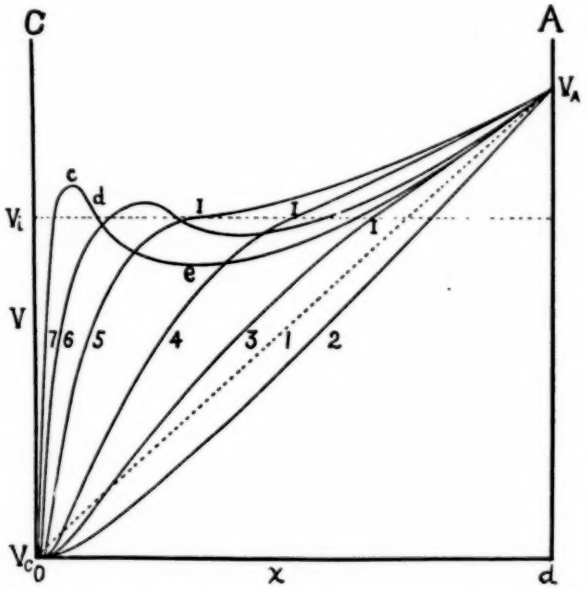

Fig. 4. The effect of increasing amounts of ionization on the distribution of potential between two parallel electrodes one of which is a source of electrons. Curve 1 shows the electrostatic distribution, curve 2 the distribution in the presence of space charge from electrons, and the remaining curves the distribution in cases of successively increasing amount of ionization at the ionizing potential V_i. (From Compton, Turner and McCurdy.)

heard. This is roughly the frequency of the flashes. It is to be noted also that these flashes only occurred in the positive column. Examined by the aid of a rotating mirror they appeared very bright from anode to Faraday dark space, where they disappear. The light of the negative glow is entirely uniform.

The question of the origin of the oscillations is a puzzling one. It seems possible that they orignate in the Faraday dark space. A small bar magnet moved about in the vicinity of the discharge had very slight effect except in the region of the Faraday dark space where its motion changed the oscillation frequency very markedly.

[8] Aston and Kikuchi, Proc. Roy. Soc. A98, 50 (1920).

In their theory of the glow discharge, Compton, Turner, and McCurdy[9] have shown the possibility of a reversed field in the region of the negative glow, especially in cases where there is large ionization. As shown in Fig. 4, increasing ionization leads finally to the potential distribution shown in curve 7. There is no reason to suppose conditons should not become even more exaggerated until the potential of the gas in the negative glow should actually be higher than the potential of the gas in the negative end of the positive column. Compton and Eckert[10] have shown this possibility for the case of the low voltage arc. The suggestion seems reasonable that this reversed field is the cause of the ionic oscillations. The positive ions fall through the potential gradient at the cathode end of the positive column with gradually increasing speed, in spite of numerous collisions, until they run into the reversed field which sends them back toward the anode. A back and forth motion of the positive ions results which constitutes the ionic oscillation.

[9] Compton, Turner and McCurdy, Phys. Rev. **24**, 597 (1924).
[10] Compton and Eckert, Phys. Rev. **25**, 139 (1925).

THE CONDUCTIVITY OF A HIGH FREQUENCY DISCHARGE IN HYDROGEN*

By Charles J. Brasefield
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Abstract

Measurements were made of the voltage between electrodes necessary to produce a current of 100 milliamperes in the discharge for gas pressures between 0.005 mm and 1.0 mm and for frequencies of oscillation between 1.25 and 20 million cycles per second (wave-lengths between 240 and 15 meters). It was found that the discharge has its maximum conductivity when operated at a frequency of 15 million cycles (20 meters) and a pressure of 0.015 mm. A theory of the mechanism of the high frequency discharge indicates that under these conditions, an electron makes an inelastic collision with a gas molecule every electronic mean free path having been under the influence of the electric force for one half cycle. The theory also indicates that for any frequency of oscillation greater than 15 million cycles, both the electric force and the gas pressure for which the conductivity is a maximum, will increase directly with the frequency of oscillation.

Introduction

THERE are essentially two methods by which a high frequency discharge can be obtained in a rarefied gas without the use of internal electrodes. The first method consists in surrounding the discharge tube by an inductance coil through which high frequency currents are passed. In the second method, high frequency voltages are applied to external electrodes of sheet metal which are attached to the outside of the discharge tube. As for the first method, it has been shown [1,2,3] that unless the high frequency currents in the inductance coil are very large, (such as are obtained with damped oscillations), the electric forces producing the discharge are principally the electrostatic forces between the ends of the coil. In other words, for small currents the two methods of excitation are fundamentally the same. On the other hand, the second method has the advantage of greater simplicity and flexibility. For this reason, the second method was used in the work about to be described.

It is well known that a high frequency discharge is profoundly affected by changes in gas pressure and frequency of oscillation. It therefore should be of interest to discover at what pressure and frequency of oscillation the discharge will function most efficiently. One way of doing this would be to study the variation in the striking potential or the minimum maintaining potential of the discharge as the pressure and frequency of oscillation are

* Publication of the Research Organization of the Grigsby-Grunow Company, Chicago, Illinois.

[1] J. S. Townsend and R. H. Donaldson, Phil. Mag. **5**, 178 (1928).

[2] C. J. Brasefield, Phys. Rev. **34**, 1392, 1627 (1929).

[3] K. A. MacKinnon, Phil. Mag. **8**, 605 (1929).

varied. Hayman[4] has made such measurements for helium and neon while C. and H. Gutton[5] have done the same for hydrogen. In some preliminary experiments the writer attempted to reproduce Guttons' results, but found that it was practically impossible to make any reliable measurements of the striking potential of the discharge because of the difficulty in determining at just what potential the discharge struck. In an effort to obtain results which would have more significance, the problem was attacked from a different angle. It was proposed to study the conductivity of the discharge, that is, the voltage between electrodes necessary to produce a given current in the gas. Such an investigation would clearly show under what conditions the high frequency discharge operates most efficiently.

Apparatus and Procedure

The apparatus used to produce the high frequency oscillations was essentially the same as that described in a previous paper.[6] The discharge tube was 90 cm long, 4.5 cm internal diameter while the electrodes surrounding it were of sheet copper 4 cm wide. It was found that the conductivity of the discharge could be measured with greatest accuracy when the distance between electrodes was 40 cm. If the electrodes were much farther apart than this then there was an appreciable leakage current between the high potential electrode and the standard used to support that end of the tube. On the other hand, if the electrodes were too close together, the capacity current between electrodes became appreciable. For pressures below 0.2 mm a continuous flow of pure hydrogen was maintained through the tube while above 0.2 mm the gas was stagnant.

Instead of applying the total voltage of the high frequency generator to the electrodes, one electrode was connected to ground through a 0–120 high frequency milliammeter. The experimental procedure consisted simply in measuring the voltage between electrodes which was necessary to produce a current of 100 milliamperes through the tube, for different frequencies of oscillation and different gas pressures. The voltage between electrodes, which is equal to the voltage across one of the condensers of the tank circuit, was calculated from the formula $E = I/2\pi fC$ where I is the tank current in amperes, f the frequency of oscillation and C the capacity in farads of one of the two equal tank condensers. The tank current was measured by a 0–10 Weston radio frequency ammeter (thermocouple type) which is guaranteed by the makers to be accurate within one percent of full scale deflection. The amplitude of the electromotive force between electrodes is $E(2)^{1/2}$. Measurements were made for frequencies of oscillation corresponding to 15, 20, 25, 30, 40, 50, 60, 80, 100, 120, 160, 200, and 240 meters.

Results

Fig. 1 shows, for a few typical frequencies of oscillation, the relation between gas pressure, and the voltage between electrodes which is necessary to

[4] R. L. Hayman, Phil. Mag. **7,** 586 (1929).
[5] C. and H. Gutton, Comp. Rend. **186,** 303 (1928).
[6] C. J. Brasefield, Phys. Rev. **35,** 92 (1930).

produce a current of 100 milliamperes through the tube. Fig. 2 shows the variation with frequency of oscillation of the minimum voltage necessary to produce a current of 100 milliamperes. It can be seen from Fig. 2 that the high frequency discharge in hydrogen has its maximum conductivity at frequencies of oscillation between 10 and 15 million cycles (i.e. between 20 and 30 meters) and at gas pressures between 0.035 and 0.015 mm. Operating the discharge under these conditions of maximum conductivity, it was possible to obtain a current as large as 300 milliamperes at 20, 25, and 30 meters. This current was, of course, limited only by the output of the high frequency generator.

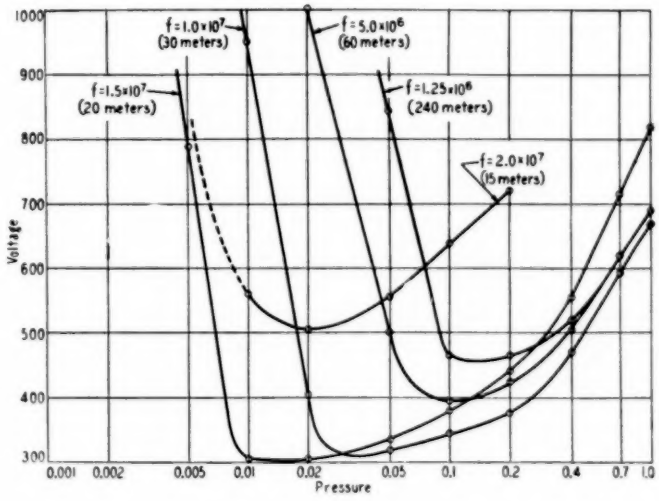

Fig. 1. Variation with gas pressure (in mm of mercury) of the voltage between electrodes necessary to produce a current of 100 milliamperes.

It can be seen from Fig. 1 that at very low pressures, the discharge is most conducting when operated at 20 meters. Using this frequency of oscillation and applying the full voltage of the high frequency generator to the electrodes it was found possible to obtain a faint white luminous discharge at pressures even as low as 10^{-6} mm. This discharge was accompanied by a blue fluorescence of the glass at the ends of the tube and by a red fluorescence of the glass at irregular spots along the tube. These spots were evidently due to bombardment of the walls of the tube by a stream of electrons for they could be shifted by moving one's finger in their neighborhood or by the presence of a magnet. The discharge itself at these low pressures seemed to be due to a beam of electrons moving along the axis of the tube, for it could be deflected by the presence of one's finger. However, no peculiarly shaped luminous bodies of gas such as Wood[7] observed using ultra high frequencies, were ever seen.

[7] R. W. Wood, Phys. Rev. **35**, 658 (1930).

Discussion

It is not difficult to explain, qualitatively, the shape of the curves of Fig. 1. In order to maintain a stable high frequency discharge, the electrons in the discharge must satisfy two conditions. In the first place, they must produce positive ions by collision with gas molecules within a distance which is in general not greater than a few electronic mean free paths and within a time which is not greater than one-half the period of the oscillation. The second condition is, of course, that at the time of collision, the electron must have a

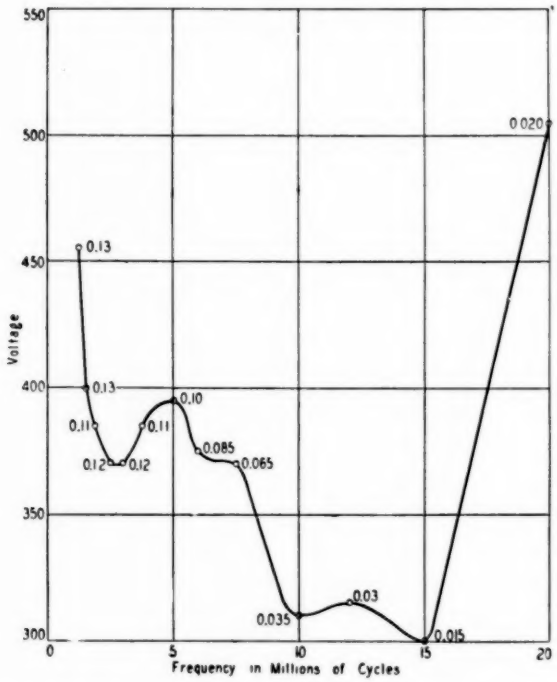

Fig. 2. Variation with frequency of oscillation of the minimum voltage necessary to produce a current of 100 milliamperes. Numbers along curve represent the pressure corresponding to the minimum voltage.

velocity sufficient to ionize a gas molecule. Now at relatively high pressures, the mean free path of the electron is small. Hence if an electron is to attain ionizing velocity in this small distance, the applied electric force must be large. On the other hand, at low pressures the mean free path of the electron is large, so that the electric force must be large in order that the electron can make a collision with a gas molecule within one-half the period of the oscillation. Between these two extremes will be a pressure at which a smaller electric force will enable the electron to satisfy the two conditions simultaneously. These points of maximum conductivity are shown in Fig. 1.

To explain the variation in the conductivity with the frequency of oscillation (Fig. 2) requires a more detailed study of the mechanism of the high

frequency discharge. The motion of an electron in a high frequency electric field can be represented by the equation

$$mx'' = eE_0 \sin 2\pi ft \tag{1}$$

where E_0 is the amplitude of the electric force and f is the frequency of oscillation. Integrating, we get the velocity at any time t,

$$v_t = \frac{e}{m}\frac{E_0}{2\pi f}(1 - \cos 2\pi ft) \quad (v_0 = 0). \tag{2}$$

Integrating once again, we get the distance the electron goes in time t

$$d = \frac{e}{m}\frac{E_0}{4\pi^2 f^2}(2\pi ft - \sin 2\pi ft). \tag{3}$$

From Eq. (2) it is evident that for a given E_0 and f, the electron will have its maximum velocity after a time $t = 1/2f$, that is, after it has been under the influence of the electric force for one half cycle. If this terminal velocity is sufficient to ionize a gas molecule and if the distance which the electron has gone in one half cycle (given by Eq. (3)) is at least one mean free path, then the high frequency discharge will be operating under the most favorable conditions possible.

Let us consider the mechanism of a high frequency discharge operating at a frequency of 20 million cycles per second (15 meters). The electron velocity given by Eq. (2) must also satisfy the equation

$$\tfrac{1}{2}mv^2 = eV \tag{4}$$

where V is at least 16 volts. As a matter of fact, a previous investigation[6] has shown that to maintain a stable high frequency discharge in hydrogen, the electron velocity must probably be at least 21 equivalent volts. Assuming this value for V and substituting the corresponding value of v in Eq. (2), we find that an electric force of amplitude $E_0 = 9.7$ volts per cm acting on an electron for one half period ($t = 1/2f$) will give it enough energy to ionize a hydrogen molecule. This, then, is the minimum electric force capable of maintaining a discharge at 15 meters; moreover, a discharge will not occur for this value of E_0 unless the distance gone by the electron is at least one mean free path. Substituting $E_0 = 9.7$ in Eq. (3) we find that the distance which the electron goes in one half period is 3.39 cm. From Fig. 2 we see that the pressure corresponding to maximum conductivity at 20 million cycles is 0.02 mm. The electronic mean free path at this pressure is 3.5 cm, which compares favorably with the distance 3.39 cm which the electron goes in one-half period.

Hence we have shown that at 20 million cycles the high frequency discharge in hydrogen has its maximum conductivity at 0.02 mm pressure because at this pressure a minimum electric force of amplitude 9.7 volts per cm is sufficient to allow an electron to make an inelastic collision with a hydrogen molecule in one mean free path having been under the influence of the elec-

tric field for one half cycle. At this point of maximum conductivity the potential difference between electrodes is 505 volts. Dividing this by the distance between electrodes, 40 cm, and multiplying by $2^{1/2}$ we get an apparent electric force of amplitude 17.8 volts per cm. This is entirely compatible with the theoretical value of 9.7 volts per cm. For the potential difference between electrodes consists of two parts. The first is the drop in potential in the body of gas and the second is the drop in potential at the electrodes. Since there is at present no means of estimating the magnitude of this second factor, all that can be said is that the apparent electric force represents the upper limit of the true electric force in the gas.

Let us now consider a high frequency discharge operating at 15 million cycles per second (20 meters). Assuming as before $V = 21$ volts, we find that a minimum electric force of amplitude $E_0 = 7.3$ volts per cm acting on an electron for one half period will give it enough energy to ionize a hydrogen molecule. Substituting this value of E_0 in Eq. (3), we find the distance which the electron goes in one half period is 4.53 cm. This compares favorably with the electronic mean free path of 4.65 cm at the pressure corresponding to maximum conductivity at 15 million cycles. Moreover, the electric force at 15 million cycles is less than the electric force at 20 million cycles. This explains why the conductivity of the discharge is greater at 15 million cycles.

At both 20 and 15 million cycles, we have seen that the mechanism of the high frequency discharge under conditions of maximum conductivity consists in an electron making an inelastic collision with a gas molecule every electronic mean free path having been under the influence of the electric force for one half cycle. If this were also the mechanism of the discharge at frequencies less than 15 million cycles, then we would expect to find that both the voltage and pressure corresponding to maximum conductivity would be less than at 15 million cycles. Since Fig. 2 shows that at frequencies less than 15 million cycles, both the voltage and pressure corresponding to maximum conductivity are greater than the voltage and pressure at 15 million cycles, we must conclude that the mechanism of the discharge at frequencies less than 15 million cycles is different from the mechanism at frequencies greater than 15 million cycles. Using Eqs. (2) and (3) we find that the difference in mechanism is due primarily to the fact that below 15 million cycles, the electron makes an inelastic collision before it has been under the influence of the electric force for an entire half period. The shape of the curve of Fig. 2., combined with a rough calculation, suggests that between 15 and 12 million cycles the electron makes an inelastic collision having been under the influence of the electric force for one third cycle; between 12 and 10 million cycles for one fourth cycle; between 10 and 7.5 million cycles for one fifth cycle; between 7.5 and 6.5 million cycles for one sixth cycle; between 6.5 and 5 million cycles for one seventh cycle; between 5 and 3 million cycles for one eighth cycle; and between 3 and 1.25 million cycles the electron makes an inelastic collision having been under the influence of the electric force for only one ninth cycle. Since the time during which the electron is under the influence of the electric field is becoming shorter, the electric force must be increased in order

that the electron can attain ionizing velocity. On the other hand, it is evident that the even fractions of a cycle will be more efficient in producing ions than the odd fractions. This explains the maxima and points of inflection of Fig. 2.

If the conditions described in the last paragraph give a true picture of the mechanism of the discharge at frequencies below 15 million cycles, then the number of electronic mean free paths involved in an inelastic collision increases as the frequency of oscillation decreases. Thus for maximum conductivity at 10 million cycles, the electron makes an inelastic collision in a little more than one mean free path; at 5 million cycles in about 3 mean free paths; and at 1.25 million cycles in about 15 mean free paths.

The reason for the sharp break in the curve at 15 million cycles is probably due to the fact that 0.015 mm pressure is the lowest pressure at which sufficient ions can be produced to sustain a current of 100 milliamperes. Hence if the current through the tube were decreased, we might expect to find maximum conductivity at some frequency less than 15 million cycles and some pressure less than 0.015 mm. As yet, experiments have not been undertaken to verify this.

In conclusion, it has been shown that the conductivity of a high frequency discharge in hydrogen is greatest when the frequency of oscillation is 15 million cycles per second and the gas pressure is 0.015 mm because the discharge is operating most efficiently under these conditions. For, under these conditions, an electron is undisturbed for one complete half cycle of the electric field, and at the end of this time it has gone exactly one mean free path so that it can make an inelastic collision with its maximum velocity. Moreover, even though at 20 million cycles and 0.02 mm pressure, the mechanism of the discharge is the same (i.e. the electron goes exactly one mean free path in one half cycle) the electric force required is greater than at 15 million cycles. Finally, at frequencies of oscillation greater than 20 million cycles, if the mechanism of the discharge is the same as at 15 and 20 million cycles (which appears very probable), it is possible to predict from Eqs. (2) and (3), first, that the electric force at maximum conductivity will increase directly with the frequency of oscillation and second, that the gas pressure at maximum conductivity will also increase directly with the frequency of oscillation.

The writer wishes to express his appreciation to the Grigsby-Grunow Company of Chicago, Illinois, for whom this investigation has been carried out. He is also indebted to several members of the Department of Physics for their interest in this work and especially to Mr. J. S. Owens who assisted in the experimental work.

ON THE CATHODE OF AN ARC DRAWN IN VACUUM

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(Received December 23, 1929)

Abstract

It has been found that the cathode is the only electrode which contributes vapor for the maintenance of an electric arc under very low gas pressure.

The velocity of this vapor was determined by two methods. Method 1 consisted of measuring the force of reaction of the vapor on the cathode and the rate of vaporization of the cathode material. Method 2 consisted of determining the force exerted by the vapor on a vane suspended in front of the cathode spot and the rate of vapor condensation on the vane.

Both these methods gave a vapor velocity of the order of 16×10^5 cm/sec. A temperature of around 500,000° K results when this value for the cathode vapor velocity is substituted for c in the equation: $\frac{1}{2}mc^2 = 3\ KT/2$.

Introduction

A SERIES of experiments with electric arcs drawn in vacuum indicated that a jet of high-speed vapor is ejected from the cathode region of such an arc.[1] A description will be given in the following paper of an attempt to obtain quantitative data on the velocity of this cathode vapor.

For the sake of simplicity the word "vacuum arc" will be used as representing an electric arc under an air pressure of the order of a few microns. The exact pressure will be given in each particular case wherever this is of interest.

Description of Experiments

An electric arc can be drawn even in very high vacuum by separating two metal contacts carrying current of the order of a few amperes.

The arc is drawn initially in the vapor given off by the vaporization of the metal at the point of last contact[2] and may be maintained by the vapor which after contact separation continues to be given off from the contact surface.

A number of preliminary experiments suggested that a jet of metal vapor with considerable velocity was emitted from the cathode region. A knowledge of the velocity of this vapor jet is not only of value in connection with the determination of the temperature of the cathode region, but will also enable us to get a better quantitative picture of the conditions in the vacuum arc in general. Accordingly an investigation was undertaken based upon the following experiments:

1. Measurement of the force of reaction of the vapor on the cathode. Knowing the amount of metal vapor evaporated per unit time the velocity can be calculated.

[1] R. Tanberg, Nature, Sept. 7, 371 (1929).
[2] J. Slepian, Journ. A.I.E.E., October, 1926, p. 930.

2. Determination of the momentum imparted by the vapor to a vane suspended in front of the cathode. Knowing the amount of vapor condensed on the vane per unit time the vapor speed can be obtained.

In Fig. 1 is shown the apparatus used for the tests outlined under #1 above. The copper cathode, *c*, consisted of a short copper cylinder, 0.6 cm

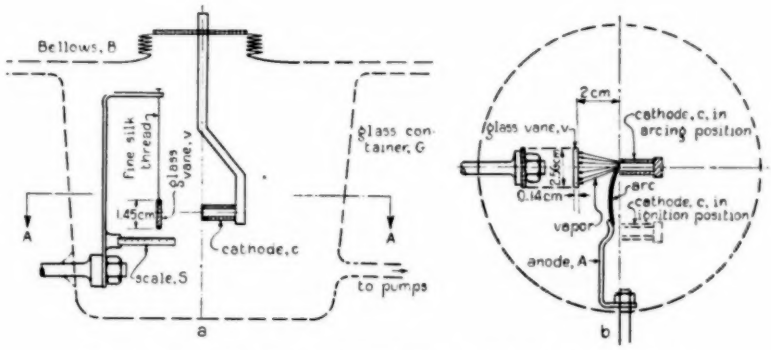

Fig. 1. Apparatus for determination of cathode vapor speed.

diameter, on the end surface of which the cathode spot was located. A quartz tubing fitted tightly around the copper cylinder in order to limit the motion of the cathode spot. The cathode was fastened to a strip of aluminum which was suspended by two fine molybdenum wires from a suitable supporting frame mounted directly on the negative terminal leading through the wall of

TABLE I. *Results of vapor speed determinations by cathode reaction tests.*

1 Test	2 Arc current (amps)	3 React. force (uncorr.) (gm)	4 Electrostatic force (gm)	5 Electrodynamic force (gm)	6 Total correction for electrodynamic and electrostatic forces grams	7 % of uncorr. react. force
353	11	198×10^{-3}	6.1×10^{-3}	4.8×10^{-3}	+ 1.3	0.66
352	16	265×10^{-3}	8.9×10^{-3}	10.3×10^{-3}	− 1.4	0.53
354	19	367×10^{-3}	10.6×10^{-3}	14.5×10^{-3}	− 3.9	1.06
355	19	367×10^{-3}	10.6×10^{-3}	14.5×10^{-3}	− 3.9	1.06
356	32	485×10^{-3}	18.0×10^{-3}	41.0×10^{-3}	−23.0	4.7

8 React. force (corr.) (gm)	9 gm/sec. evap. from cathode	10* $(C^2)^{1/2}$ cm/sec.	11 T° abs. temper. at cathode
199.3×10^{-3}	0.17×10^{-3}	16.3×10^{5}	6.8×10^{5}
263.6×10^{-3}	0.25×10^{-3}	14.6×10^{5}	5.45×10^{5}
363.1×10^{-3}	0.30×10^{-3}	16.8×10^{5}	7.25×10^{5}
363.1×10^{-3}	0.30×10^{-3}	16.8×10^{5}	7.25×10^{5}
$462.\times10^{-3}$	0.49×10^{-3}	13.1×10^{5}	4.37×10^{5}

* Based upon figures in column 8 and 9.

the arcing chamber. The pressure in the arcing chamber varied between 0.2×10^{-3} mm Hg at the beginning of the arcing to around 10×10^{-3} mm Hg at the finish. The arc current was supplied to the cathode through an iron wire which dipped into a pool of mercury, *P*, electrically connected with the negative terminal.

Thus the cathode was suspended so it would swing freely back and forth in a plane vertical to the cathode surface. The deflection was measured on a scale, S, located underneath the cathode. The instrument was calibrated for cathode deflecton against the corresponding force on the cathode surface.

The arc was formed by contact between the cathode and anode as indicated in Fig. 1b. As soon as the arc was playing the anode was moved to about 1.5 m away from the cathode. The deflection of the cathode during the arcing was of considerable magnitude and quite steady and could, therefore, be read with good accuracy on the scale provided for that purpose.

The results of a series of typical tests are compiled in Table I. Column 3 gives the force on the cathode as a function of the arc current given in column 2. Column 9 gives the amount of vapor in grams per second leaving the cathode during the arcing.

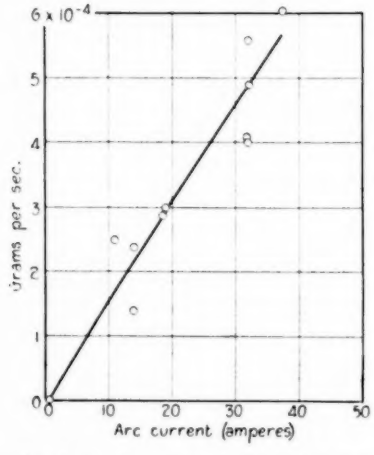

Fig. 2. Vaporization of copper cathode by arc in vacuum.

These last values are taken from the curve in Fig. 2 which is based upon a separate series of tests made under identically the same conditions as those existing during the measuring of the cathode reaction force. The cathode was weighed before and after each test and the time duration of the arcing was noted, thus determining the rate of vaporization of the cathode material.

Column 10 contains the root mean square velocities of the vapor leaving the cathode, calculated from the data given in columns 8 and 9 using the formula:-

$$(C^2)^{1/2} = 1.39K/m$$

where K = force in dynes on cathode.

m = mass in grams per second of metal evaporated from the cathode.

$(C^2)^{1/2}$ = root mean square velocity in cm/sec. of vapor leaving the cathode.

The development of this formula will be found in the appendix to this paper.

Considering the conditions under which the tests were made it is evident that the results should be corrected for possible radiometric, electrodynamic and electrostatic forces. A discussion of these corrections can also be found in the appendix.

The values of the cathode reaction force obtained when the above mentioned corrections are taken into account will be found in column 8 in Table I.

As will be seen later by the calculation of the corresponding temperature, the vapor velocities obtained are very high compared with what could be expected from conservative estimates of the temperature existing at the cathode. It was, therefore, thought desirable to check the results by the vane deflection method already referred to.

This was made with the apparatus shown in Fig. 3a and b. The cathode, *c*, was of the same design (copper cylinder surrounded by quartz tube) as

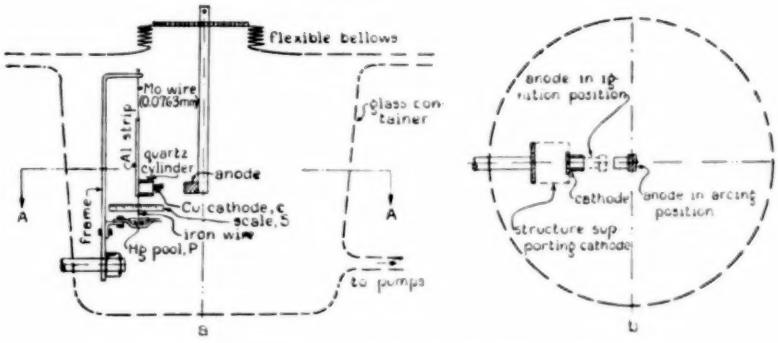

Fig. 3. Apparatus for measuring cathode vapor speed.

used in the previous experiments. It was fastened to a metal rod which could be moved from outside the vacuum by means of the flexible bellows, *B*. The same pressure was maintained during these experiments as during the cathode reaction tests just described. The arc was formed by moving the cathode to touch the anode as indicated in Fig. 3b. As soon as the arc was playing, the cathode was moved back in front of the glass vane, *v*, consisting of a square piece of Pyrex glass. This was suspended by two fine silk threads from a supporting frame indicated in the figure. The deflection of the vane was read directly on the scale, *S*, and the force necessary to deflect the vane as a function of the deflection was determined.

During a test the arc would play between the cathode and anode as indicated in Fig. 3b, while the vapor would be projected from the cathode spot directly against the vane deflecting this according to the momentum imparted to it by the impinging molecules.

The presence of this jet of high-speed vapor was not only evident from the definite deflection of the vane, but could also be realized visually by the sharply defined, faintly luminous, cone-shaped region, extending from the cathode spot to the vane. The results of these tests are given in Table II.

TABLE II. *Results of vapor speed determination by deflecting vane method.*

1 Test	2 Arc current (amps.)	3 Force on vane (gm)	4 Vapor condensed (gms/sec.) on vane	$(C^2)_{\frac{1}{2}}5$ cm/sec. R.M.S. vapor velocity
366	14.2	64×10^{-3}	42.6×10^{-6}	20.8×10^{5}
369	16.0	64×10^{-3}	53.7×10^{-6}	16.6×10^{5}
367	18.0	94×10^{-3}	65×10^{-6}	20.1×10^{5}

The velocities in column 5 in this table were calculated by the same formula as previously used for calculating the vapor velocities from the cathode reaction tests, while m (column 4), representing the amount of metal vapor condensed on the vane per second, was obtained from the curve in Fig. 4, which is based upon direct measurements. It will be seen that the values for the cathode vapor speed obtained by this method agree quite well in the order of magnitude with the values obtained by the previous method.

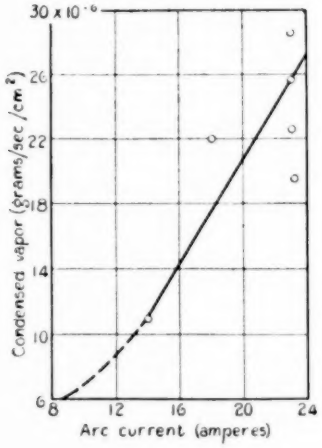

Fig. 4. Condensation of copper vapor on collector 2 cm from cathode.

When judging these results it must be remembered that it is practically impossible to prevent the cathode spot from traveling on the cathode surface. The amount of vapor hitting the vane may, therefore, vary somewhat with the location of the cathode spot.

The discussion in the appendix of possible corrections to these measurements will show that the effects from radiometric pressure, electrostatic fields etc., can be entirely neglected.

CALCULATION OF TEMPERATURE CORRESPONDING TO THE MEASURED VAPOR VELOCITIES

The knowledge of the speed with which the metal vapor is ejected from the cathode region enables us to calculate at least the order of magnitude of the temperature at the cathode by the well-known relations between the average

kinetic energy and the absolute temperature of the molecules in a gas. It is believed to be justified to use in this connection the equation applying to three degrees of freedom of the molecule:

$$\tfrac{1}{2}m' \cdot C^2 = 3kT/2 \qquad (1)$$

where m' is the molecular mass in grams; C^2 is the mean square of the velocity of the molecules in cm/sec.; K is Boltzmann's gas constant in erg/°Abs. and T is the absolute temperature.

The justification for using this form of the temperature-kinetic energy equation is the good agreement it gives with experimental results when applied to Stern's[3] and Eldridge's[4] measurements on velocities of molecules emitted from a hot metal surface under low gas pressure.

Substituting in Eq. (1) the values for the molecular velocities given in Table I give temperatures as shown in column 11.

General Discussion of Results

As will be realized, these temperatures are far in excess of even the most extreme temperatures ever measured in connection with any physical phenomenon of any duration. One must, however, remember that the space close to the cathode of an electric arc constitutes a very small volume with a large energy input where one, from only conservative estimates, could expect exceedingly high temperatures.

A similar case with large energy input into a small space constitutes the interesting experiments made by J. A. Anderson[5] with electrically exploded wires, during which he obtained estimated temperatures of 300,000°C.

Conclusion

The temperature existing at the cathode spot determined from the velocity of the cathode vapor is of the order of 500,000°K.

If this extreme temperature is confirmed by other investigators, our present ideas of what takes place at the cathode of a vacuum arc must be revised. The cathode region would then offer an excellent opportunity to study the very interesting physical conditions which must exist in a location with such an enormous temperature.

The writer wants to express his thanks to Dr. J. Slepian for the encouragement he has received from him during the preparation of this paper.

APPENDIX

Calculation of vapor velocities. A molecule will exert an impulse

$$\int K'dt = m' \cdot u \qquad (2)$$

[3] Stern, Zeits. f. Physik **2**, 49 (1920).
[4] Eldridge, Phys. Rev. **30**, 931 (1927).
[5] J. A. Anderson, Astrophys. J. p. 37. Jan. (1920).

on any surface which it is either leaving or striking. In this equation:

K' = force in dynes.

m' = mass in grams of the molecule.

u = component of velocity of molecule in cm/sec. perpendicular to surface.

The probability that a molecule in the vapor shall have a velocity component lying between u and $u+du$ is: $f(u).\ du$ assuming a certain velocity distribution. If n is the number of molecules per cm³ of the vapor, the number of these which has a velocity laying between u and $u+du$ is: $n.f(u).du$. The total number of molecules per cm² per second leaving the cathode region with velocities lying within this particular interval must therefore be:

$$\Delta\gamma = u(n \cdot f(u) \cdot du) \cdot \text{molecules/sec.} \tag{3}$$

where u = velocity perpendicular to the surface in cm/sec.

The force exerted by these molecules on the cathode per cm² is (from Eqs. (2) and (3)). $K' = (m' \cdot u) \cdot (u \cdot n \cdot f(u) \cdot du)$.

$$K' = m' \cdot n \cdot u^2 \cdot f(u) \cdot du. \tag{4}$$

The total force per cm² of molecules leaving the cathode:

$$K = m' \cdot n \int_0^\infty u^2 \cdot f(u) \cdot du. \tag{5}$$

By changing integration limits:

$$K = m' \cdot n \cdot \tfrac{1}{2} \int_{-\infty}^{+\infty} u^2 \cdot f(u) \cdot du.$$

If u^2 denotes the mean square of the velocity component perpendicular to the surface:

$$K = \tfrac{1}{2} m' \cdot n \cdot u^2. \tag{6}$$

Since the vapor density $m' \cdot n$ is not practical to determine it is necessary to express this term by the amount of vapor leaving the cathode. The total number of moles per cm² leaving the cathode per second is found by integrating Eq. (3) from 0 to ∞ : $\gamma = n\int_0^\infty u.f\ (u.)\ du$.if $|\bar{u}|$ denotes the average numerical value of the perpendicular component of velocity we have: $\gamma = \frac{1}{2} n \cdot |\bar{u}|$. Thus the total mass of the atoms leaving the cathode per second is: $A.m'.\gamma = A.m'.(\frac{1}{2}n.|\bar{u}|) = m$ or

$$A \cdot m' \cdot n = 2\frac{m}{|u|} \tag{7}$$

where m is total loss of cathode material during one second of arcing and A is the area of the cathode spot in cm². Making Eq. (6) apply to the whole

[6] Richardson, "The Emission of Electricity from Hot Bodies" Edition 1921, pages 155 and 177.

cathode spot by multiplication with the cathode spot area "A" and combining it with Eq. (7) gives

$$K = (\overline{u^2}/|\bar{u}|m). \tag{8}$$

There is reason[6] to believe that the fundamental equations of Maxwell's velocity distribution theory can be used in connection with the conditions considered here. We can, therefore, substitute in equation (8) $\bar{u}^2 = \frac{1}{3}\overline{C}^2$ and $|\bar{u}| = \frac{1}{2}\overline{C}$ which gives: $K = \frac{2}{3}C^2,/C\ (C^2)^{1,2}\ m\cdot$according to the Maxwellian velocity distribution function:

$$(C^2)^{1/2}/C = 1.08.$$

Hence:

$$(C^2)^{1/2}1.39K/m \tag{9}$$

which is the formula used for calculating the values given for the root mean square velocities in columns 10 and 5 in Tables I and II respectively.

The conditions at the vane are somewhat more complicated than assumed above because the existence of a Maxwellian velocity distribution in the gas at the vane surface may be questioned. However, the application of Eq. (9) to the data obtained from the vane deflection experiments will undoubtedly give values representing the correct order of magnitude of the R. M. S. velocity of the vapor striking the vane.

The values given in column 5 Table II which are calculated from Eq. (9) must therefore only be considered as serving the purpose of a rough check on the velocity values given in Table I.

Discussion of Possible Corrections to Vane Deflection Tests

a. Radiometric effect—Due to the brilliancy of the cathode spot it was thought possible that the deflection of the vane during the experiments may have been affected by radiometric pressure. The tests recorded in Table III indicate, however, quite conclusively that the effect of radiometric pressure on the vane deflection must be of such small magnitude as to be negligible.

Table III. *Showing that variations in gas pressures do not affect the deflection of the vane.*

1 Test	2 Arc current (amps.)	3 Distance cathode-anode (cm)	4 Pressure (mm Hg) before test	4 Pressure (mm Hg) after test	5 Force on vane (gm)	Remarks
456	2.30	2.0	0.9×10^{-3}	56×10^{-3}	94×10^{-3}	vane deflect.
457	"	"	63×10^{-3}	64×10^{-3}	130×10^{-3}	did not vary
458	"	"	0.2×10^{-3}	13×10^{-3}	130×10^{-3}	with press.
459	"	"	0.2×10^{-3}	12×10^{-3}	94×10^{-3}	increase
460	"	"	0.2×10^{-3}	16×10^{-3}	130×10^{-3}	
461	"	"	0.2×10^{-3}	8.5×10^{-3}	130×10^{-3}	

During these experiments the gas pressure was measured by a McLeod gauge before and after each test allowing sufficient time for the pressure to equalize all through the vacuum system. The time required for equalization

was very short since all tube connections were dimensioned so as to give a large ratio of diameter to tube length.

The pumps were shut off during each experiment. Since the leakage of the system was found to be negligible, the increase in pressure during each test represents gas given off from the electrode during the arcing.

Thus during test #456 which lasted several seconds the pressure increased from 0.9×10^{-3} mm Hg to 56×10^{-3} mm Hg but the deflection of the vane remained constant around the value given in column 5 in spite of the fact that the radiometric effect within the same pressure interval according to data by Westphal[7] should be expected to increase ten fold.

The difference in pressure at the end of tests 460 and 457 in Table III does not reveal any change in the force on the vane while the corresponding change in radiometric pressure according to Westphal's experiments should be about 28 percent.

A similar analysis of the other tests recorded in Table III points just as conclusively to the fact that the radiometric pressure on the vane can be entirely neglected during the writer's experiments.

b. Accumulation of charge on vane. If the vapor consisted of ions of one sign it would charge the vane up to a potential of the same sign as the charge on the vapor particles. The magnitude of this charge would increase until a sufficient field was set up to reflect the vapor particles back against the cathode. The momentum imparted to the vane by the vapor under such conditions would be about twice the momentum delivered to the vane if the particles condensed. It is, therefore, necessary to determine if such a reflection actually can have taken place during the tests recorded in the Tables I, II and III.

During a series of experiments the vapor from the cathode spot was made to condense on a metal plate which was kept under different potentials relative to the cathode. The metal plate was located in the same relative position to the cathode and anode as the vane during the previous experiments. The potential was varied between 0 and +60 volts without producing any effect upon the amount of condensed vapor.

Since the R. M. S. velocity of the vapor (15×10^5cm/sec.) corresponds to about 74 volts assuming singly-ionized Cu atoms, this potential interval should have been sufficient to show some changes in condensation had the vapor when reaching the vane been charged.

Corrections to Cathode Reaction Tests

a. Radiometric effect: From the discussion in connection with the vane experiments it is probably safe to assume that the radiometric effect is negligible also at the cathode outside of the cathode spot proper. This assumption is justified on account of the extremely steep temperature gradient existing at the cathode spot which will limit the high temperature area to the spot itself.

[7] Westphal, Zeits. f. Physik **1**, 92 (1920).

It remains, however, to be proved that the radiometric pressure at the cathode spot also will be of such small magnitude as to be negligible.

Knudsen[8] gives the following formula for the radiometric force as a function of temperature and gas pressure:

$$K = \frac{1}{2} p \cdot \left(\frac{T_1}{T_2} - 1 \right) \tag{10}$$

where K is the radiometric force in grams/cm^2; p is the gas pressure in grams/cm^2, and T_1 and T_2 are absolute temperatures.

The good agreement obtained by Knudsen between experimental and calculated values within the pressure range existing during the writer's arcing experiments justifies the use of this formula in calculating the radiometric force at the cathode of the vacuum arc.

Assuming a temperature at the cathode of 700,000°K and a temperature of the surrounding parts of 300°K gives:

$$K = 328 \times 10^{-3} \text{ grams/cm}^2$$

from Eq. (10) for a pressure equal to 10×10^{-3} mm Hg. If we assume that the current density of 7200 amp/cm^2 found by Güntherschultze[9] for cathode spots on iron under atmospheric pressure also holds for a vacuum arc the cathode spot of a 20 amp. arc will have an area of 2.8×10^{-3} cm^2. Thus the total force on the cathode spot due to radiometric effects under the conditions specified will not exceed 0.92×10^{-3} grams/cm^2.

A comparison with the forces actually measured on the cathode spot shows that the radiometric effect also in this case can be entirely neglected.

b. Electrostatic force on the cathode. On account of the cathode drop an electrostatic force will be exerted on the cathode during the arcing in such a direction as to tend to move it into the arc. Since the cathode drop is known to be concentrated in a very small distance from the cathode surface the electrostatic force may be of such magnitude that it can not be neglected.

If S is the area in cm^2 over which the electric field extends at the cathode and E the field strength in absolute units per cm, the force in dynes exerted on the cathode is (assuming a dielectric constant = 1) $F = S \cdot E^2/8 \cdot \pi$.

Observations of the Stark effect[10] indicates a field strength at the cathode surface of the order of 10^5 volts/cm. Since the field at the edge of the cathode spot probably falls off very rapidly it should be correct to substitute for S in the above equation the area of the cathode spot determined from the current density observed by Güntherschultze.[9] The values thus obtained are given in column 4 Table I.

c. Electrodynamic forces. Due to the form of the current path in the apparatus shown in Fig. 1 an electrodynamic force can be expected to act upon the suspended cathode during the arcing, tending to increase its deflection. The correction for this will be found in column 5, Table I.

[8] Knudsen, Ann. d. Physik **32,** 809 (1910).

[9] Güntherschultze, Zeits f. Physik **11,** 74 (1922).

[10] R. Seeliger, Physik der Gasentladungen, Leipsig, p. 282 (1927).

THE REFLECTION OF LITHIUM IONS FROM METAL SURFACES

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Abstract

A study has been made of the reflection of lithium ions from reflectors of platinum foil and of nickel crystals deposited on tungsten foil. Movable ground joints in the tube were completely eliminated in order to prevent contamination of the reflector surfaces by grease. Readings were taken with both cold and hot reflectors. Spodumene was used as a source of ions and reflection was studied in the meridian plane only.

Superposed on a diffuse scattering of ions were two reflected beams. One was reflected nearly specularly, as found by Read and by Gurney, the angle of maximum reflection, however, being idependent of accelerating potential. The other beam appeared only at voltages above 200 and was composed of ions most of which had retained 80 percent or more of their original energy. This beam was found between the incident beam and the normal to the surface, at angles independent of the accelerating potential up to 700 volts. This independence of angle on voltage forbids diffraction interpretations. A tentative explanation consists in supposing specular reflection from the (110) planes of the nickel crystals, but the agreement is not entirely satisfactory.

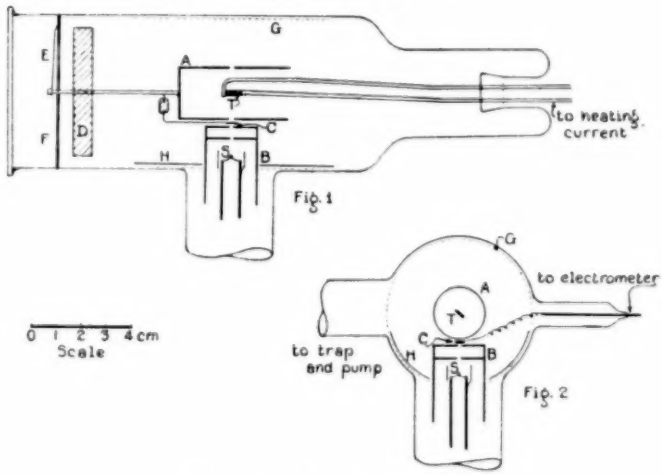
THE reflection of lithium and potassium ions from a platinum surface has been investigated by Read,[1] and that of lithium, potassium, and caesium from platinum by Gurney.[2] Both found considerable reflection from a clean platinum surface, the maximum occurring at an angle somewhat larger than that corresponding to specular reflection. Since an extremely clean reflector seemed to be necessary in order to obtain appreciable reflection, it was desirable to continue the study, making every effort to avoid contamination of the reflector, especially by grease vapor. The discovery of electron diffraction by crystals[3] and the work of Ellett and Olson[4] on reflection of neutral atoms by crystals suggested a trial of crystal surfaces as reflectors of positive ions.

Apparatus

The tube used is shown in Fig. 1 and Fig. 2. A tiny crystal of spodumene, S, on an electrically heated platinum strip was used as a source of lithium ions.[5] These were accelerated to the drum, B, and a portion passed through holes 1 mm in diameter, and entered the cylinder, A, which had a 3 mm slot cut around it to admit them. After striking the reflector, T, those ions which

[1] Read, Phys. Rev. **31,** 629, (1928).
[2] Gurney, Phys. Rev. **32,** 467 (1928).
[3] Davisson and Germer, Phys. Rev. **30,** 705 (1927).
[4] Ellett and Olson, Phys. Rev. **31,** 643 (1928).
[5] Read, reference 1, p. 629.

were reflected at any given angle could be caught by the collector, *C*, which was a 2 mm×7 mm nickel strip rigidly fastened by means of a Pyrex bead to the axis of the cylinder, *A*. The collector-cylinder system was mounted in a supporting framework (not shown in the figure) so that it could be rotated from the outside of the tube by an electromagnet applied to the soft iron armature, *D*. The angle at which the collector was set was indicated by a pointer, *E*, moving over a graduated circle, *F*. The collector was connected to a string electrometer by a flexible lead. The positive ion current from the collector was balanced by a negative current from an ionization chamber.[6] The central part of the tube was shielded by a gauze, *G*, and an additional screen, *H*, of sheet metal was placed around the bottom part of the tube in order to prevent the escape of any positive ions from the source except



Figs. 1, 2. Construction of tube.

through the holes in the top of the drum, *B*. The cylinder and framework supporting it were grounded through the same lead as the screen, *H*, but the gauze, *G*, had a separate ground connection. Neither of these ground leads is shown in the figure. Tungsten wires were used for sealing through the Pyrex.

The reflector was either a 5/16 in.×3/8 in. strip of platinum-iridium foil (10 percent iridium) 0.0005 in. thick, or a 1/8 in.×3/8 in. strip of tungsten foil, kindly supplied Dr. W. E. Forsythe, upon which nickel crystals had been deposited by evaporation, according to the method of Rupp.[7] He states that the minute crystals so formed are oriented with their (111) planes parallel to the surface of the backing foil. The platinum foil was mounted so as to be kept always under slight tension by a tungsten spring, while the heavy nickel wires supporting the nickel crystal reflector had enough elasticity to keep the tungsten foil taut. In either case the reflector could be heated electrically to any temperature desired. Except as otherwise noted, all metal parts were made of nickel.

[6] Read, reference 1, p. 630.

[7] Rupp, Ann. d. Physik **1**, 801 (1929).

Spodumene proved to be so satisfactory a source of lithium ions that the stem supporting the source and drum was sealed permanently into the side tube. A useful life of from 75 to 100 hours for one crystal was not unusual. One end of the main tube was ground off and closed by a glass plate waxed on with ordinary red sealing wax, care being taken to keep the wax on the outside of the tube. Contamination by grease vapors was thus entirely eliminated and that by vapors of wax reduced to a very small amount.

Originally a small Faraday cylinder was used as a collector. It was found that the measured ion current to such a cylinder was sensibly the same no matter whether the ions struck the inside of the cylinder or the bottom outside. It has been noted by others[8] that the reflection of positive ions almost disappears at normal incidence. Furthermore, a particularly clean surface seems to be necessary to secure much reflection at any angle, and no pains were taken to secure this degree of cleanliness of the collector. Hence, since the ions would be incident normal to the collector and the collector was not especially cleaned, one would not expect loss of ions by reflection even from a simple strip. Experience bears out this conclusion. The cylinder was later replaced by a strip because it took up less space.

Method

The accelerating potential could be applied in two parts: one between the source and the drum, the other between the cylinder and the reflector, drum and cylinder both being grounded. The field between cylinder and reflector served both to accelerate primary ions moving toward the reflector and to retard reflected ions leaving it. Thus by making the source 30 volts positive and the reflector 20 volts negative with respect to the drum and cylinder, the ions caught by the collector would have struck the reflector with an energy of 50 volts and would have retained 20 volts or more after impact. These will be designated as 50–20 volt ions.

It is true that with this arrangement the ions are in a field of force while they are being reflected and this may conceivably influence the reflection somewhat. The geometry of the tube was such that the field between the cylinder and the reflector was, to a rough approximation, radial, and the velocities of the reflected ions should not have been greatly altered by it as regards direction. Furthermore, when a reading was being taken the field around the cylinder was not distorted by the presence of the collector, since its potential at such a time was always zero. One disadvantage of this method is that the field between the cylinder and the reflector focuses the incident beam to some extent, so that even though the ion current getting through the holes in the drum remains constant, the number of ions striking the reflector is greater the greater the potential difference between it and the cylinder. Thus for the higher retarding potentials, i.e., larger fractions of total accelerating potential applied between cylinder and reflector, the current to the reflector is actually increased.

[8] Gurney, reference 2, p. 472, and his quotation of Jackson, Phys. Rev. **28,** 524 (1926).

An alternative method would be to keep the drum, cylinder, and reflector all at ground potential, applying the whole accelerating field between the source and the drum, and the retarding field between the cylinder and collector. This has two disadvantages. In the first place, the field in the immediate vicinity of the collector tends to change the direction of approaching ions, deflecting them so that some which should strike the collector now miss it entirely. In the second place, this method involves placing the whole collector-electrometer system at a positive potential, sometimes comparatively high, with the consequently greater likelihood of insulation leaks. All of the data in this paper were obtained with the first arrangement.

The procedure in taking a series of readings was as follows. The desired accelerating and retarding potentials were applied and the source was heated for several minutes until the emission became steady. The total ion current getting through the holes in the drum was measured by turning the collector so as to cover the holes. This current was kept as nearly constant as possible and was checked occasionally during a run, little difficulty being found in maintaining constancy. The heating current through the reflector was adjusted to give the desired temperature and the collector then rotated so as to collect ions reflected at various angles. The width of the collector subtended an angle of about 9.5° at the center of the reflector, and in taking readings settings were made at 10° intervals. The pressure was kept as low as possible, being of the order of 10^{-6} mm. If the reflector were at any temperature higher than that of a just visible red heat, it was found necessary to apply to it a negative potential of 2 or 3 volts in order to suppress positive ion emission from the reflector itself.

Results

In general, the reflector gave more intense reflection when hot than when cold, though little change was observed as the temperature was raised beyond a medium red. In most of the following work a medium red heat was used. It is probable, as Read and Gurney suggested, that the increased reflection when hot was due to the removal of surface films of gas or grease. Read reported that within a few seconds after the heating current was turned off no reflection could be detected, while Gurney publishes a curve showing that the intensity of reflection decreased to 0.4 of its initial value during the first minute after heating was stopped. With the tube used in this investigation it was found that the intensity was 0.9 of its original value after an interval of 8 minutes, in one instance, and even after 20 minutes it had sunk only to 0.86 I_0.

When only small retarding fields were applied so that ions of all but the very lowest velocities were collected, reflection was found as shown in Figs. 3–6. The figures show the incident beam coming from the right, and the length of the radius vector from the center of the reflector to any point on a curve is proportional to the intensity of reflection at that angle. The broken lines marked N and S show, respectively, the normal to the surface and the angle of specular reflection.

The reflection from platinum, Fig. 3, shows much the same sort of distribution as reported by Read and Gurney, but there are several points of difference. Apparently there was considerably more diffuse scattering at small

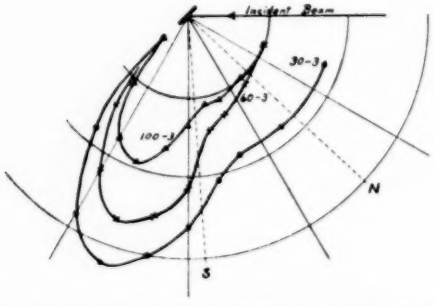


Fig. 3. Reflection from platinum, angle of incidence 43°. Small retarding potentials.

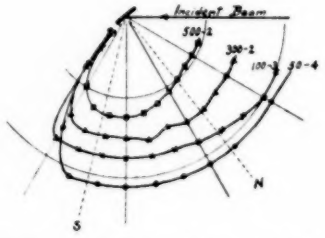


Fig. 4. Reflection from nickel, angle of incidence 51.5°. Small retarding potentials.

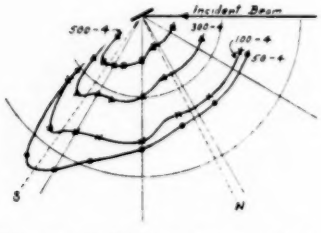


Fig. 5. Reflection from nickel, angle of incidence 62.5°. Small retarding potentials.

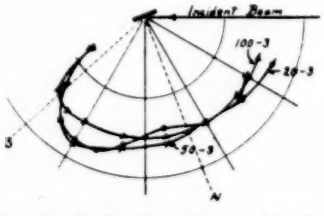


Fig. 6. Reflection from nickel, angle of incidence 69°. Small retarding potentials.

angles than was found by either Read or Gurney. There is a rather broad peak in each curve, the maximum falling at a larger angle than specular reflection would give. Contrary to the findings of Read, the position of this maximum did not change with a change in the accelerating potential.

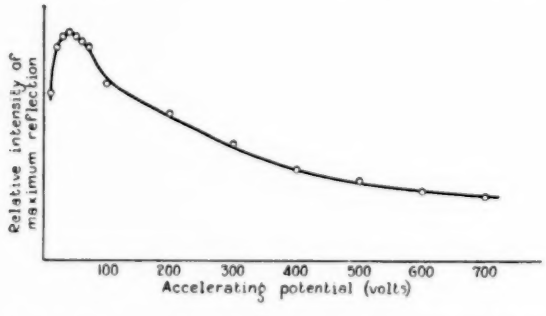


Fig. 7. Reflection from nickel, angle of incidence 62.5°.

The curves for a nickel crystal reflector, Figs. 4–6, show hardly any peaks in some cases. Where they do occur they are not as prominent as with the platinum reflector, and fall much more nearly at the specular angle.

The relation between the intensity of the maximum and the accelerating potential is shown in Fig. 7 for a nickel reflector with a primary beam incident at 62.5°. The maximum in the neighborhood of 40 volts agrees with the results of Read and Gurney for platinum.

Figs. 8–13 are curves for larger retarding potentials. These curves show directly the angular distribution of all reflected ions having more than a certain amount of energy. For instance, the 50–20 volt curve of Fig. 8 shows the distribution of ions which originally had an energy of 50 volts and which retained 20 volts or more after reflection. For low accelerating potentials these curves show a progressive shift of the maximum toward larger angles as the retarding potential is increased, indicated in Fig. 8. This shows that the ions which were the least deviated from their original directions were apt to have higher velocities than those which were deflected through larger angles. This corroborates the result obtained by Gurney.

From a set of curves such as Fig. 8 or Fig. 9 it is possible to get some idea of the velocity distribution of the ions as well as their distribution in angle.

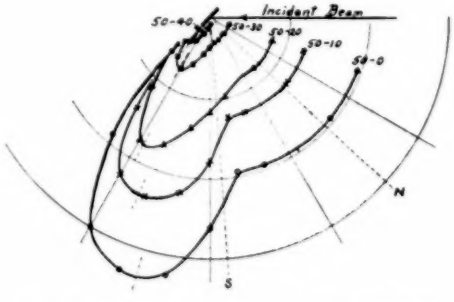


Fig. 8. Reflection from platinum, angle of incidence 43°. Large retarding potentials.

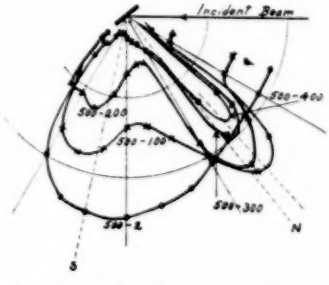


Fig. 9. Reflection from nickel, angle of incidence 51.5°. Large retarding potentials.

Thus in Fig. 9 it is seen that there is a fairly well-defined beam of ions coming off at an angle just inside the normal to the surface, and the ions composing the beam seem to have retained a large part of their original energy. The fact that some of the curves for large retarding potentials show a greater intensity than those for smaller retarding potentials at a given angle may be explained by the focusing effect of the field between the cylinder and the reflector, as before mentioned. Increasing the retarding potential accentuates the specularly reflected peak, though reducing its intensity, at the same time bringing into marked prominence the high velocity beam which must previously have been obscured by general, low velocity scattering. It should be noted that the position of this new peak, as shown in Figs. 10–13, is unaffected by a change in the accelerating potential of the incident ions up to 700 volts, the largest used. This is not particularly apparent in Fig. 11. While the number of voltages used for an angle of incidence of 62.5° was not as large as might be desirable to locate accurately the position of the new peak, careful examination of all the data taken leads to the conclusion that the maximum was located at about 5° inside the normal, as shown by the 250–150 volt curve.

However, the accuracy of measurement was hardly sufficient to locate the maximum within 5°.

The peak near the normal was not observed with accelerating voltages below 200 volts and increased in prominence as the accelerating potential was raised. Its position so near the normal to the surface at once suggested that it might be due to the condensation of ions upon the surface and their subsequent evaporation, according to the theory of Langmuir[9] and Frenkel.[10] This would result in a cosine distribution with a maximum along the normal. However, it would hardly be expected that the ions would evaporate with such high velocities as were observed, if, indeed, they evaporated as ions at

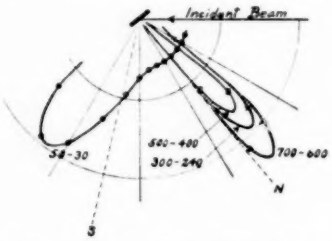


Fig. 10. Reflection from nickel, angle of incidence 51.5°. Large retarding potentials.

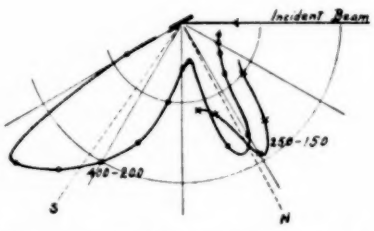


Fig. 11. Reflection from nickel, angle of incidence 62.5°. Large retarding potentials.

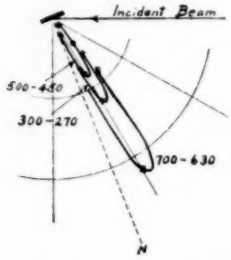


Fig. 12. Reflection from nickel, angle of incidence 69°. Large retarding potentials.

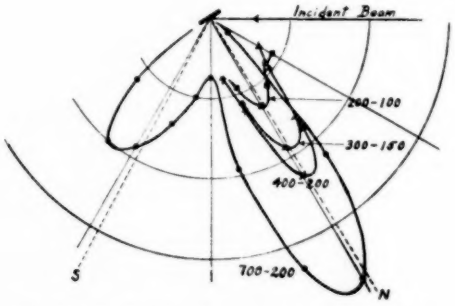


Fig. 13. Reflection from platinum, angle of incidence 59°. Large retarding potentials.

all. The sharpness of the peak, too, did not suggest a cosine law. As a further check on the adsorption—re-evaporation idea, the effect was tried of changing the density of the ion stream, since the work of Cockcroft[11] indicated that stream density was an important factor in molecular condensation. However, it seemed to be impossible to make the peak either appear or disappear simply by changing the ion current. In one trial, using a voltage below that at which the peak appeared, an increase in the current by a factor of thirty failed to produce a peak.

A hot reflector gave the effect better than a cold one. It was not observed

[9] Langmuir, Phys. Rev. **8,** 149 (1916).
[10] Frenkel, Zeits. f. Physik **26,** 117 (1924).
[11] Cockcroft, Proc. Roy. Soc. **A119,** 293 (1928).

at all with a nickel crystal reflector at an angle of incidence of 42° or with platinum at 44°.

When the larger accelerating potentials were used there sometimes appeared to be an emission of secondary electrons from the reflector. It was usually possible, by the application of a suitable magnetic field, to prevent these from reaching the collector and yet to leave the positive ions practically unaffected.

Discussion

The reflected beam of ions coming off near the normal to the surface and having nearly the same velocity as the incident ions is the most interesting result of this study. It would be most natural to try to attribute it to positive ion diffraction were it not for the fact that the position of the beam is independent of the accelerating potential. The wave-length associated with a 200 volt lithium ion would be expected to be approximately 0.01A. Although it is difficult to predict the behavior to be expected of a complex ion when it strikes a crystal surface, specular reflection would seem to be as likely as anything else. A consideration of the possibilities of such reflection from various planes in the nickel crystals shows that, of those having the largest atom densities, only the (110) planes could give specular reflection at approximately the observed angles. Table I shows the angles observed and calculated. Having no accurate knowledge of the crystal structure of the platinum reflector, it is impossible to calculate the reflection as in the case of the nickel crystals.

Table I. *Reflection from nickel crystals. All angles measured from the normal to the surface.*

Angle of incidence on (111) planes	Angle of Reflection		
	Calculated from (110) planes	Observed	Difference
51.5°	19.5°	8.5°	+11.0°
62.5°	8.5°	5.5°	+3.0°
69.0°	2.0°	9.0°	−7.0°

One argument against the hypothesis of reflection by the (110) planes is that the differences between observed and calculated values of the angles show a systematic trend in one direction. However, the number of different angles tried was not sufficient to permit drawing a definite conclusion. The reflected beam was so nearly normal to the surface as to suggest the possibility that more accurate measurements might show it to lie exactly along that direction. A rough test of the relative satisfactoriness of the two suppositions—reflection by the (110) planes or reflection along the normal—is found by applying the method of least squares, though here again a greater number of angles would be desirable. This method gives little choice between the two hypotheses, the slight difference being in favor of the first mentioned.

The writer wishes to acknowledge his indebtedness and express his appreciation to Professor A. J. Dempster, who proposed the problem and whose suggestions proved extremely valuable, and to Mr. K. S. Woodcock, who assisted in taking some of the data and making the drawings.

THE ZODIACAL LIGHT AND THE GEGENSCHEIN AS PHENOMENA OF THE EARTH'S ATMOSPHERE.*

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Abstract

A quantitative atomospheric theory of the zodiacal light and the gegenschein is developed. Neutral particles sprayed out in all directions from the earth's atmosphere are ionized at 50,000 to 70,000 km levels by the ultra-violet light of the sun. Because of the wabble of the earth's magnetic field with the rotation of the earth ions near the equatorial plane stay for some time at these high levels to form a ring around the earth, ions at high latitudes fall quickly back to the earth to give aurorae. The gravitational magnetic drift of the ions forces the ion ring into a long oval stretching out away from the sun to 10^6 km. The pressure of the sunlight warps the oval into the plane of the ecliptic and makes the ions stream out like a comet's tail. The ions are fluorescent; they absorb the sun's ultra-violet light and emit a part of the absorbed energy as visible light. The oval ring is the zodiacal light; the comet tail ion stream is the gegenschein. The zodiacal cones in December are somewhat to the south of the cones in June; the evening cone is south and north of the morning cone in March and September, respectively. These theoretical inferences are in qualitative accord with observation. The theory suggests that the spectrum of the zodiacal light and the gegenschein be different from that of sunlight.

Quantitative estimates lead to a low ion density in the zodiacal ring, less than 10^3 ions$\cdot$cm^{-3} and to a *rate of escape of the terrestrial atmosphere* of 10^6 particles$\cdot$cm$^{-2}\cdot$sec^{-1} or 10^{-6} of the entire atmosphere in 10^6 years. These are perhaps under-estimates. The theory indicates that helium escapes more rapidly than the other gases because of its lightness and higher ionization potential. This may account for the small amount of helium in the atmosphere, which is regarded as being surprisingly low in the face of the estimated large rate of supply from the earth.

Variations in the zodiacal light, from the observations of Jones in 1853–1855 and of more recent observers, *are shown to occur usually during magnetic storms.* Similarly Barnard's observations of the variations in the gegenschein fall in with magnetic disturbances, although more data are needed to establish the connection clearly. The variations are in accord with the atmospheric theory.

Introduction

SHORTLY after sunset when the evening twilight has gone the zodiacal light appears as a faint cone of light in the west rising upward from the horizon, with a similar cone in the east before dawn.[1] At their apexes the cones narrow to a band which extends across the sky from one apex to the other. Thus the phenomenon is spoken of as a "band" of luminosity. The

* Published with the permission of the Navy Department.

[1] For general descriptions of the zodiacal light and the gegenschein see Newcomb, Encyclopaedia Britannica, 13th ed., Vol. 28, page 998; Schmid, "Das Zodiakallicht," Hamburg, 1928; Bayldon, Pub. Ast. Soc. of the Pacific 12, 13 (1900); and references cited throughout the present paper.

band lies closely, but not exactly, along the plane of the ecliptic. It is usually less bright than the milky way and may be seen on any clear night when there is no disturbing illumination such as the moon, planets, the milky way, artificial lights, etc. At an angle of 30° from the sun, the closest angle to the sun at which the light can be seen when observed in the eastern or western sky, the band is about 40° wide.[2] The width of course is rather indefinite for the band is brightest near its center and fades into obscurity at the edges. Newcomb[3] and Barnard[4] in north latitudes around 45° during the midnight hours of the summer solstice observed a glow passing from the west to the east along the north horizon. They concluded that this was the zodiacal band, for it could not have been ordinary twilight because the sun was more than 18° below the horizon, and that therefore the band was about 70° wide along the sun's axis. With increasing angular distance from the sun the band decreases in width and in brightness. At 90° from the sun it is about 20° wide and at 150° about 10° wide. At 180°, the point directly opposite the sun, there is a faint knot of luminosity, sometimes appearing as a swelling in the zodiacal band, called the "gegenschein"[5]. Attempts to measure the parallax of the zodiacal band have always led to values close to zero, but, what is very curious, often negative. The parallax of the gegenschein, as determined by simultaneous observations in the northern and southern hemispheres, was found[6] to be zero within an error of 1° or 2°. Therefore the zodiacal light and the gegenschein have been considered to be far away, beyond the moon, or farther.

The zodiacal light is supposed to be sunlight scattered or reflected or emitted by particles in the plane of the ecliptic. Whether the particles come from the atmosphere or the earth or are planet dust widely scattered through the solar system is an unsettled question, although probably the planet dust theory is more generally held at the present time. Recently the physics of the outer fringe of the atmosphere[7] of the earth was developed, primarily for the purpose of the theory of aurorae and magnetic storms. At the time it was realized that the ideas might be brought to bear on the zodiacal light. Just how this was to be done was not clear until it was noticed (Hulburt, Amer. Phys. Soc. Bul. Dec. 30, 1929) that the fluctuations in the zodiacal light occurred at the same time as the magnetic disturbances. This indicated at once that the planet dust theory was open to objection and pointed the way to the development of the atmospheric theory. It is the purpose of this paper to give the evidence for the connection between the zodiacal light changes and magnetic storms and to describe a theory of zodiacal light based on the action of molecules and ions in the outer fringe of the terrestrial atmosphere. The theory offers an explanation of many features of the zodi-

[2] Hall, Monthly Weather Review **34,** 126 (1906).
[3] Newcomb, Astrophys. Jr. **22,** 209 (1905).
[4] Barnard, Astrophys. Jr. **23,** 168 (1905).
[5] Barnard, Popular Astronomy **7,** 169 (1899): **27,** 109 (1919).
[6] Scarle, Astrophys. Jr. **8,** 244 (1898).
[7] Maris and Hulburt, Phys. Rev. **33,** 412 (1929).

acal light and the gegenschein which the planet dust theory is inadequate to explain.

In company with almost all who have written about the zodiacal light we shall use extensively the classical observations[8] of Reverend George Jones USN, made for the most part in north latitudes 10° to 30° while on a voyage on the Pacific Ocean. From April, 2, 1853, to April 22, 1855, he observed the light every night, weather and other things permitting, and sketched on a chart of the heavens the zodiacal light as he saw it. The drawings, 341 in number, and their descriptions were published; they are by far the most complete and extensive series available. The observations are of gold, and whereas some writers, among them Jones himself, have wondered at apparent inconsistencies we have found that it is just these variances which fall in with the pattern of the theory, Jones wrote in his introduction, "I have put down all, exceptions and incongruities as well as others, not feeling authorized to omit any portion; for who can say, in a new science, that what seem to be exceptions are not a part of the general rule."

2. *Abnormalities in the zodiacal light and magnetic storms.* It was recognized long ago by Humboldt, Arago, Birt and others[8,9] that the zodiacal light is at times variable in intensity the entire body of the light alternately weakening for a few minutes and strengthening again. That the zodiacal light is often unusually intense during epochs of strong aurorae has been known for a long time. For example, in 1881 Groneman[9] referred to the fact as of common knowledge. Aurorae are known to occur in general during periods of magnetic disturbance, but no one has been interested in examining the exact relations with the zodiacal light. Turning to Jones' observations we find that occasionally he noticed and commented on fluctuations in the intensity of the zodiacal light; the entire body of the light grew brighter and dimmer in a period of two or three minutes. In a few cases he recorded an unusually wide spread of the zodiacal luminosity. One of his descriptions is as follows, "The changes were a swelling out, laterally and upwards, of the Zodiacal Light, with an increase of brightness in the Light itself; then, in a few minutes, a shrinking back of the boundaries, and a dimming of the Light; the latter to such a degree as to appear, at times, as if it was quite dying away; and so back and forth for about three quarters of an hour; . . . . ." We have plotted these abnormalities on a qualitative scale in dots as ordinates against the dates as abscissas; a portion of the plot is given in Fig. 1. The magnetic storms observed at The Greenwich Observatory[10] are plotted as short lines in the figure; 1, 2, and 3 mean a storm of moderate, strong and very strong intensity respectively. It is seen that the zodiacal light abnormalities occurred, usually during magnetic disturbances. To summarize the data: There were 27 magnetic storms, or groups of storms, in the period of Jones' observations, 17 of which were followed by cases of unusual zodiacal

[8] Jones, United States Japan Expedition, Vol. III, Washington, 1856. "Observations on the Zodiacal Light."

[9] Groneman, Archives Néerlandaises, Tome XVI.

[10] Maunder, Monthly Notices, Roy. Ast. Soc. **65**, 2 and 540 (1904–5).

light. There were 10 storms with no zodiacal light observations because of clouds, etc., and 10 instances when the zodiacal light might be regarded as abnormal with no accompanying magnetic storms.

A few more recent observations may be mentioned. Pachine[11] in Russia observed the zodiacal light to be remarkably brilliant and to exhibit fluctuations on January 28, 1911 at 6:30 P. M. The light appeared normal during the following days. The preceeding days were cloudy but the clouds were unusually illuminated and he concluded that the exceptional zodiacal brilliance began on the 25th. We do not know whether or not the illumination of the clouds might have been due to an aurora. A four-day magnetic storm of intensity 2 began at 4 hr, G. M. T., on January 24, 1911. Fluctuations in

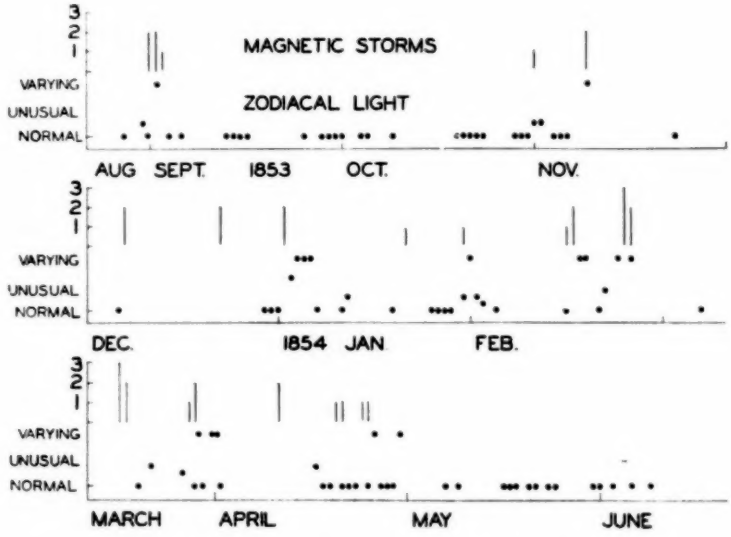

Fig. 1. The dots are the zodiacal light observations of Jones, the vertical lines are the magnetic storms.

the zodiacal light were observed by Hanahan[12] in South Carolina on February 4 and 13 and on March 5, 1913. The storms in this period were January 29 (1), February 13 (1), 24 (1), and March 13 (2). The fluctuations on February 13 fall in with a magnetic storm, the others do not. The zodiacal light was very brilliant on March 21, 1927, according to a photograph by Graff[13]. The period was one of magnetic activity, a seven-day magnetic storm lasting from March 13 to 20 of intensity 2 on March 16 and 1 on March 20. Fluctuations in the zodiacal light were seen simultaneously by two observers Kamei and Oraki[14] at widely separated points in Japan on November 3, 1929, at about 3 A. M. local time. A magnetic disturbance set in on November 2 at 23 hr,

[11] Pachine, Bul. Société Astronomique **27,** 68 (1913).
[12] See note by Glanville, Pop. Ast. **37,** 493 (1929).
[13] Graff, Grundriss der Astrophysik, page 481, Teubner, (1928.)
[14] See note by Glanville, Pop. Ast. **38,** 124 (1930).

G. M. T., rose to intensity 2 on November 3 and continued with decreasing violence through November 6.

Of course abnormalities in the zodiacal light may at times be due to local causes, such as variations in haze, etc., rather than to changes in the light itself, and in such cases there would be no connection between the zodiacal light behavior and magnetic disturbances. The foregoing facts, however, support the conclusion that the connection is genuine and this suggests that the zodiacal light is influenced by the same solar emission which gives rise to magnetic storms. All in all, the data indicated that the zodiacal manifestation occurred within less than two days after the storm began, sometimes it was observed a day or a few hours before the storm (see the theoretical discussion of section 13).

3. *The energy, polarization and spectrum of the zodiacal light.* The energy $\cdot$ $cm^{-2} \cdot sec^{-1}$ received at the earth from all the stars, from the total night sky (the non-polar aurora) and from the total zodiacal region was found[15] to be equal to that of 1440, 0.08 and 0.08 stars, respectively, of magnitude 1 on the Harvard visual scale. The energy of starlight at the earth is 3×10^{-3} erg. $cm^{-2} \cdot sec^{-1}$ and therefore that of the night sky and the zodiacal luminosity each amounts to $0.08 \times 3 \times 10^{-3} \div 1440 = 1.7 \times 10^{-7}$ erg $\cdot cm^{-2} \cdot Sec \cdot^{-1}$. Assuming the zodiacal region to occupy 10^{-1} of the area of the sky, the energy emitted per $cm^{-2} \cdot sec^{-1}$ from the zodiacal region on the average is of the order of 10^{-6} erg $\cdot cm^{-2} \cdot sec^{-1}$. This means that the zodiacal region is ordinarily about 10 times as bright as the sky would be if there were no stars.

The zodiacal light was observed to be partially polarized,[16] about 15 per cent. Early observers[17] found that the spectrum of the zodiacal light was similar to that of sunlight, as well as could be judged from visual observations. More recently Fath [18] photographed the spectrum with a 12 hour exposure, from 3 to 4 A. M. for 12 days. The spectrum from λ5000 to 3900A was 2.2 mm long. Two absorption lines could be seen on the plate. Fath wrote, "A comparison of this plate with one of the sky spectrum taken with the same slit-width shows these lines to be *G* and the blend of *H* and *K* of the solar spectrum. These are the only two lines shown on the sky comparison plate within the limits of the spectrum obtained on the zodiacal light plate. There is no indication of bright lines on any of the spectrograms of the zodiacal light. Thus insofar as spectra of such low dispersion and resolving power can be trusted, we would seem to have good evidence to support the claim that the zodiacal light is reflected sunlight."

4. *The planet dust theory of the zodiacal light.* This theory assumed that there are dust particles in a flat lens shaped region with the sun at the center spreading out in the plane of the ecliptic well beyond the orbit of the earth. The particles were not molecules of a gas, for due to diffusion and light pressure molecules would not stay near the plane of the ecliptic. The particles

[15] Van Rhyn, Astrophys. Jr. **50,** 356 (1919).
[16] Wright, Amer. Jr. of Sci. and Arts **7,** 451 (1874).
[17] Smyth, Trans. Roy. Soc. Edinburgh **20,** 489 (1852).
[18] Fath, Lick Obs. Bul. **5,** 141 (1909).

were considered to be small solid bodies each moving in its independent orbit around the sun. It was suggested that they were small meteoroids of the solar system, possibly remnants of the spray and dust from the large splash which inaugurated our planet system.[19] The particles were assumed to reflect the sunlight, particles 1 mm in diameter and 5 miles apart of albedo 0.07, the albedo of the moon, being sufficient to account for the observed zodiacal luminosity.[20] Light reflected from minerals such as granite, clay, etc., was found to be partially polarized.[16]

Since the zodiacal light undergoes fluctuations in intensity it follows that all of the light can not be reflected sunlight. For the sunlight, at least in that portion of the spectrum accessible to us, does not fluctuate very much, the short period (a few hours or a day) variations[21] of the solar constant being usually less than 10 per cent, whereas the variations in the zodiacal light intensity, although not measured, would perhaps be of the order of hundreds of percent. Therefore the planet dust theory, if it be retained at all, requires some fundamental modification not heretofore contemplated.

5. *The atmospheric theory of the zodiacal light.* As described in the following pages the atmospheric theory assumes that fast flying atoms or molecules are sprayed out in all directions from the sunlit hemisphere of the earth which, after a number of hours, are ionized by the ultra-violet light of the sun. Under the action of solar radiation pressure and the earth's magnetic and gravitational flelds ions at levels beyond 30,000 km form a sort of oblong ring around the earth approximately in the plane of the ecliptic. The ions absorb sunlight in the far ultra-violet region of the spectrum and re-emit a portion of the absorbed energy as visible light. This is the zodiacal light. This view encounters two difficulties at the outset, namely, the light might be expected to be unpolarized and the spectrum should be different from that of sunlight. The first difficulty may be got round for the present by suggesting that the fluorescence radiation might be polarized to some extent and by expressing the wish that the polarization observations be repeated. The difficulty with the spectrum is more serious, so serious in fact that if future observations show that the zodiacal spectrum is that of sunlight the atmospheric theory in the form given here will fall to the ground. We may remark that the solar corona and certain comet tails exhibited a spectrum more of less continuous which, in part at least, was not that of sunlight.[22]

6. *The ion spray to distances of 70,000 km.* In the earlier paper, reference 7, paragraph 3, it was shown that beyond 450 km above sea-level there were about 10^{-16} molecules and atoms in a $1cm^2$ column of the atmosphere. These dance up and down, being knocked upward by thermal impacts from below and falling back under gravity, with practically no collisions except at the 450 km level where they experience 10^{14} collisions per sec. The thermal ve-

[19] Jeans, "Astronomy and Cosmogony," page 400, (1928).

[20] Russell, Dugan and Stewart, "Astronomy," Vol. 1, page 359 (1926).

[21] Annals of the Astrophys. Obs. of the Smithsonian Institution, IV, pages 17 and 207 (1922).

[22] Reference 20, pages 439 and 507; Slipher, Lowell Obs. Bul. 52; etc.

locities are hardly greater than 2 km sec^{-1} and the levels reached by the particles are on the average not above 2000 km. It was assumed that 2×10^6 of the collisions were of the second kind, *i. e.* collisions with excited atoms or molecules, which gave the particles velocities as great as 10 km $\cdot sec^{-1}$ (See reference 7 for a more detailed discussion.) In the present case the assumption is extended to include 2×10^7 collisions which result in velocities as high as 12 or 13 km $\cdot sec^{-1}$. Thus 10^7 $cm^{-2}\cdot sec^{-1}$ fast moving atoms or molecules move out from the earth. They are ionized by the ultra-violet light of the sun in a time t given by the relation $t=a/I_0(1-e^{-\beta})$, (reference 7, equation (1)) where a is the ionization potential of the atom or molecule, I_0 is the energy of the sun in the ionizing wave-lengths and β is the atomic absorption coefficient. β is defined in the usual way by

$$I = I_0 e^{-\beta y x}, \tag{1}$$

where I is the intensity of the light after passing through x cms of atoms or molecules of density y. It is assumed that the sun is quiet, i.e. no aurorae or

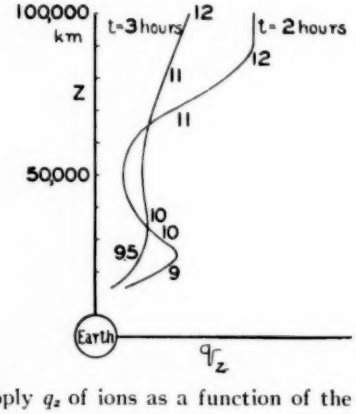

Fig. 2. The rate of supply q_z of ions as a function of the distance from the earth.

magnetic storms, and that its spectrum is that of a black body at 6000° K. The energy in the region from 725 to 750A of the solar spectrum falling $cm^{-2}\cdot sec^{-1}$ on the earth is 10^{-4} erg. With this value for I_0, with $\beta=3\times10^{-11}$ and with $a=3.1\times10^{-11}$ ergs, corresponding to 20 volts, t is 3 hours.

Assuming always 3 hours for the time of ionization, the heights z where the neutral atoms were ionized were calculated for various values of v the velocity of projection from the 300 km level of the earth's atmosphere. For example, an atom with $v=9.7$ km $\cdot sec^{-1}$ reaches $z=31{,}800$ km in 2.6 hours and falls back to 31,400 km in 0.4 hours where it is ionized; with $v=10$, 10.3 and 11 km $\cdot sec^{-1}$ the atoms are ionized at $z=39{,}800$, 48,000 and 70,000 km respectively. The v, z curves were plotted for $t=3$ hours and $t=2$ hours. Assuming that the velocities are equally distributed among the high flying atoms, in which case the number of atoms with a specified energy is proportional to the square root of the energy, the rate of production q_z of ions cm^{-3} was determined from the slopes of the v,z curves. The q_z,z curves are given

in Fig. 2 for $t = 2$ and 3 hours, q_z being in arbitrary units; the numbers written along each curve are the values of v of the atom which became ionized at the ordinate z. It is seen that q_z is greater at heights above 50,000 km than at lower heights. Since v can not go on increasing indefinitely q_z must grow less somewhere and we may assume that q_z reaches a maximum between 50,000 and 80,000 km and falls to low values at greater distances. The foregoing calculations can only be regarded as illustrative, but they serve to show that hypotheses, perhaps not unreasonable ones, of the sort which have been made lead to a rate of ion production which does not fall off rapidly with increasing z and which may even increase with z for a time.

In order to determine the distribution of the high flying ions around the earth it is assumed that the number of fast moving atoms or molecules emitted from each cm² of the surface of the high atmosphere in a direction ϕ is proportional to $\cos\phi \cos i$, where ϕ is the angle with the normal to the surface

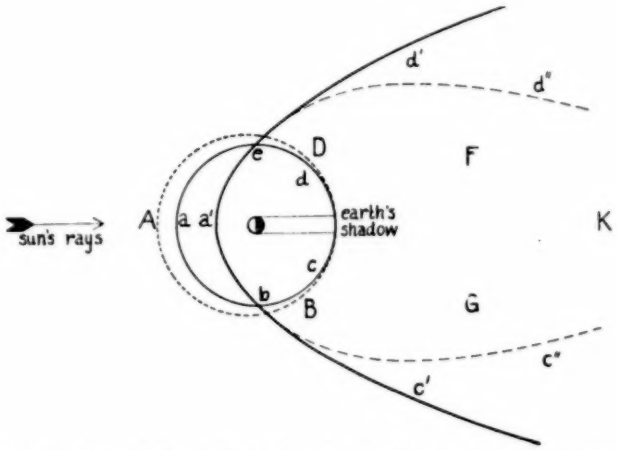

Fig 3. Cross section of the zodiacal ion ring in the plane of the earth's equator.

and i is the angle of incidence of the sunlight on the surface. Let q_θ be the total number of fast moving particles emitted from the day hemisphere in a direction at an angle θ with the sun's rays. The relation between q_θ and θ is thus the same as that which expresses the distribution of light reflected from a perfectly diffusing hemisphere or the variation of the intensity of moonlight with the phase of the moon. The relation is

$$q_\theta = q_0(1 + \cos\theta)/2, \tag{2}$$

where q_0 is the value of q_θ for $\theta = 0$. The q_θ, θ curve is a cardioid. In Fig. 3, *abcde* is a circle around the earth in the plane of the equator with a radius of 50,000 km. From this circle as a base q_θ, calculated from (2), is measured outward and forms the curve ABD. This curve represents the rate of supply of high flying atoms and molecules, and hence of ions, at the high levels in the plane of the equator. Rotating the curve about AK as an axis forms a figure which represents the rate of supply of the high flying ions around the

earth. Although (2) is an approximation, it is exact enough for our purposes. It assumes that the radius of the earth is small compared to 50,000 km, thereby neglecting the earth's shadow and giving values of q_θ greater than zero in the shadow, except for $\theta = 180°$. No ions can be formed in the shadow but ions can get there because some fast flying atoms shoot over the poles of the earth, become ionized and follow along a magnetic line into the shadow.

7. *The ion ring around the earth.* It is assumed that the earth is electrically neutral at all points. Therefore any electric fields which exist are generated by the ions themselves and the motions of the ions at distances beyond several radii of the earth are approximately independent of the rotation of the earth on its axis[23], i.e. are the same whether the earth rotates or not. The centrifugal force due to the motion of the earth in its orbit around the sun is small and is neglected. When the neutral particles are ionized the ions and electrons thus formed are guided by the earth's magnetic field. They fall

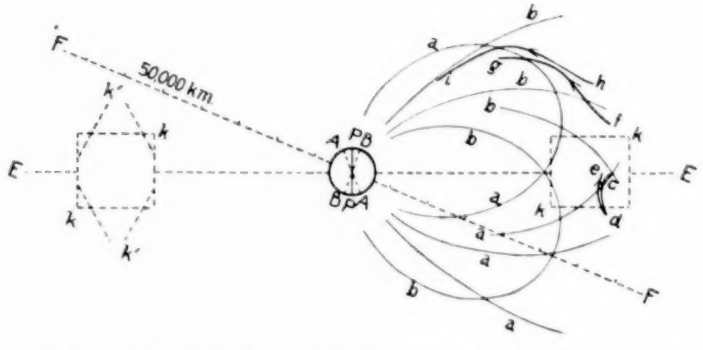

Fig. 4. A section in the plane through the center of the earth normal to the sun's rays; *kk* or *k'k'* is the zodiacal ion ring.

toward the earth along the magnetic lines of force under gravity and they drift across the magnetic field because of gravity, the positive ions going east and the negative electrons west. Dealing first with their fall we take into account the wabble of the magnetic field with the rotation of the earth. The magnetic axis makes an angle of about 20° with the geographic axis; the fact that the magnetic pole does not pass exactly through the center of the earth is of no consequence in the present discussion. In Fig. 4 *PP* is the geographic axis, *AA* is the magnetic axis with its magnetic lines given by curves *a* and *BB* is the magnetic axis 12 hours later with its magnetic lines *b*. The figure is in the plane through the center of the earth normal to the sun's rays. *EE* marks the plane of the earth's equator, and *FF* and *EE* mark the plane of the ecliptic at equinox and solstice, respectively; the angle between *EE* and *FF* is 23°. At equinox *PP* is in the plane of the drawing of Fig. 4, at solstice *PP* is tilted 23° out from the plane of the drawing.

An ion at *c*, Fig. 4, with an initial zero velocity component along the magnetic field *H*, falls under gravity along a number of slightly different curved

[23] Page, Phys. Rev. **33**, 823 (1929).

paths depending on the time of day at which it starts to fall. One of the curved paths is given by *cde*, Fig. 4; the ion reaches *e* after about a day, and takes roughly a week to fall 20,000 km. Although the general path is *cde*, the actual path may be a spiral with a radius ρ which depends upon v, the velocity component across H, according to

$$\rho = mv/He. \tag{3}$$

m and e are the mass and charge of the ion, respectively; electromagnetic units are used throughout the paper. At 50,000 km with $v = 10$ km $\cdot$ sec^{-1} ρ is 50 km for a nitrogen atomic ion, and is less for lighter ions as helium. Therefore ρ is small compared to the distances under consideration and in general the ions move along their paths in relatively tight spirals. An ion at *f*, Fig. 4, falls along the path *fg* reaching *g* in 1 day; an ion at *h* falls along *hi* and reaches the earth in less than a day. Thus the speed with which ions leave any level is a minimum on the earth's equator *EE* and increases rapidly on either side of *EE*. Since the rate of supply of ions at any level in the plane of Fig. 4 is constant the ion density y at a given level is a maximum at *EE* and falls off on either side by perhaps an order of magnitude or more at 20° from *EE*. Further, ions formed at the, say, 30,000 km level will remain there a shorter time than those formed at the 60,000 km level because of the greater gravitational attraction of the earth at the lower levels. This combined with the rate of supply curves of Fig. 2 indicates that the ion density y in the levels below 50,000 km down to perhaps 20,000 km may be much less than from 50,000 to 70,000 km.

Therefore the ions congregate into a ring around the earth lying roughly in the plane of the equator on the daylight side of the earth; on the night side, as is shown in sections 9 and 10, the ring is warped off the equatorial plane approximately into the plane of the ecliptic and is stretched out into a long oval by light pressure and by magnetic gravitational actions. Illustrative equivalent cross-sections of the ring at $\theta = 90°$ are shown by *kk*, Fig. 4. These are sketched 20° wide and 20,000 km deep, the actual cross-section is perhaps more like *k'k'*, Fig. 4; at $\theta = 0°$ the width is about 70° (section 9).

The total number of ions y_1 in any cross-section of the ring 1 cm thick is equal to $q_\theta t$, where t is the time the ions remain there. Since t is a constant with respect to θ we have from (2)

$$y_1 = y_0(1 + \cos\theta)/2, \tag{4}$$

where y_0 is the value of y_1 at $\theta = 0$. An outflow of 10^7 high flying atoms cm^{-2} $\cdot$ sec^{-1} from the earth means a supply of 10^5 ions and electrons $\cdot$ cm^{-2} $\cdot$ sec^{-1} into the portion of the ring nearest the sun, i.e. $q_0 = 10^5$. If t is ten days or 10^6 sec. there are 10^{11} ions in an average 1 cm^2 column out through the ring. With an equivalent cross section 20,000 km wide and 20,000 km deep the average ion and electron density y is 50, and y_0 is 2×10^{20}. At $\theta = 90°$ $y = 25$ and $y_1 = 10^{20}$. With such low densities there are practically no collisions, for the free path of an ion is 10^{14} cm. The ion densities are so low that it seems doubtful that the presence of the ions and electrons could be detected by experiments

with wireless waves. It also seems doubtful that the diamagnetism[24] of the ions has any great effect upon the earth's magnetic field in the zodiacal region, although the field may be distorted to some extent.

It is assumed that ions absorb the solar ultra-violet radiation from λ900 to 1000A, or an equivalent amount. The energy received at the earth in this spectrum region is 1 erg·cm^{-2}sec^{-1}, as calculated for a quiet sun at 6000 K. Assuming the atomic absorption coefficient β for the radiation to be 10^{-12}, the energy absorbed by the 10^{11} ions is 10^{-1} erg·sec^{-1}. If 10^{-5} of the absorbed energy is emitted as visible light the ion ring emits 10^{-6} erg·cm^{-2}·sec^{-1}, which is the observed value of the zodiacal luminosity (section3).

8. *Radiation pressure.* The numerical assumptions of section 7 lead at once to a value for the radiation pressure on the zodiacal ions. The force of the radiation on y ions of mass m is myp, where p is the acceleration. If the energy flux of the radiation is I_0 the energy absorbed by the y ions is $I_0\beta y$ and the energy density of the absorbed radiation is $I_0\beta y/c$, where c is the velocity of light. Then $myp = I_0\beta y/c$, or

$$p = I_0\beta/mc. \tag{5}$$

With $I_0 = 1$ erg·cm^{-2}·sec^{-1}, $\beta = 10^{-12}$ and $m = 2.3\times10^{-23}$ grams, as for a nitrogen atomic ion, p is 1.5 cm·sec^{-2}. For helium and hydrogen atomic ions p is 5.2 and 20.8 cm·sec^{-2}, respectively. The solar gravitational acceleration g_s is 0.6 cm·sec^{-2} at the earth. Therefore p is greater than g_s by perhaps an order of magnitude. This in keeping with the observed streaming away in the direction of the sun's rays of the particles in comets' tails. The motion indicated that in some cases the radiation repulsion was 12 times the solar gravitational attraction.[25]

In this paper we do not encounter any ionic velocities so great that the absorption coefficients and radiation pressure are influenced by Doppler effects, as Milne[26] found in dealing with stellar atmospheres. We may state without giving the calculations that light pressure and scattering effects calculated from the Rayleigh scattering formula are entirely negligible compared to the absorption and fluorescence processes which we have assumed.

Atomic absorption coefficients of order 10^{-11} or 10^{-12} as assumed in sections 6 and 7 may be too high, although one can not be very sure about it. Various theories[27] indicate values of β of order 10^{-15} to 10^{-17} near the heads of the principal series of hydrogenic atoms. Observations[28] on the lines and continuous spectrum near the heads of the principal series of the alkali metals give β of the order of 10^{-19}. In the ozone molecular band[29] β is 10^{-17} at about 2500A, and in the oxygen molecular band β is greater than 10^{-17} at 1500A,

[24] Gunn, Phys. Rev. **33,** 614 (1929), equation (12).

[25] Chambers, "The Story of the Comets," page 37, 1910.

[26] Milne, Monthly Notices, Roy. Ast. Soc. **86,** 459 (1925–26).

[27] Kramers, Phil. Mag. **46,** 836 (1923); Eddington, "The Internal Constitution of the Stars," equation 166.8; Pannekoek, K. Akad. Ansterdam, Proc. **29,** 1165 (1926); etc.

[28] Mohler, Phys. Rev. Sup. **1,** 216 (1929), and references therein.

[29] Fabry, Proc. Phys. Soc. London **39,** 1 (1926).

as judged from Lyman's[30] spectrograms of the oxygen band. One can not be very certain that these values of β give a correct idea of the order of magnitude of β in the far ultra-violet for the atmospheric atoms, which are probably helium, nitrogen and oxygen. However, in the present case we are not restricted to a definite as sumption about β; we require that the product βI_0 have certain specifiedvalues. If β should be less than 10^{-12} we can increase the assumed value of I_0, which is of course permissable within limits.

9. *The ion ring on the side of the earth near the sun is compressed toward the earth and on the side away from the sun is stretched out to a great distance.* It has been shown[7] that long free path ions, no matter what their velocities are, under the combined action of gravity and the earth's magnetic field move at right angles to these two vectors with a velocity w given approximately by

$$w = mg \sin \phi / He, \tag{6}$$

the positive ions going eastward and the negative ions and electrons westward. ϕ is the angle between g and H; w is a maximum at the equator and decreases rapidly at high latitudes. The drift of the ions and electrons constitutes an electric current flowing eastward around the earth if the circuit is complete. If the circuit is not complete electric fields are built up which react on the motion of the ions. At the surface of the earth $w = 4.6$ cm $\cdot$ sec^{-1} for a singly charged nitrogen atomic ion at the equator, and is 1/26,000 of this or practically zero, for the electron. The eastward current i, due to the drift velocity w, is $i = y_1 ew$ where y_1 is the total number of ions in a cross-section of the ring 1 cm thick in a plane passing through the earth's axis. Since g and H are proportional to z^{-2} and z^{-3}, respectively, z being the distance to the center of the earth, $w = 4.6z/z_0$, where $z_0 = 6400$ km is the radius of the earth, and $i = 4.6ezy_1/z_0$. With $e = 1.59 \times 10^{-20}$

$$i = 1.14 \times 10^{-28} z y_1. \tag{7}$$

We note in passing that this current causes a negligibly small magnetic field at the earth. With $y_1 = 2 \times 10^{20}$ and $z = 50{,}000$ km, i from (7) is 10^3 amperes. The current causes a magnetic field at the earth less than 10^{-5} gauss, which is probably inappreciable.

In order that the zodiacal ion ring be in a steady state the drift current i must be a constant through all cross-sections of the ring. Therefore from (7) zy_1 should be a constant. The values of y_1 are given by (4) and hence

$$z = A/(1 + \cos \theta), \tag{8}$$

where A is a constant. The z, θ curve from (8) is the curve for the steady state and is shown by $c'ba'ed'$, Fig. 3. The branches bc' and ed' meet at infinity. This is wrong; actually they join at a finite distance. The error arises from the fact that (8) is derived through (4) from (2) which gives no ions at $\theta = 180°$. As explained in section 6 there are ions at all values of θ, and hence z in (8) is always finite. Therefore, the branches of the steady state

[30] Lyman, Astrophys. Jr. **27**, 87 (1908).

curve will be something like *bc''* and *ed''*. The curve is quite different from the circular ring *abcde* in which the ions are produced. Therefore the ions immediately and continually flow from the circle to distribute themselves in the curve *c''ba'ed''* although because of radiation pressure they probably never attain this distribution. The process is similar to that worked out[31] for the ions in the lower atmospheric levels from 100 to 200 km and is as follows:

Suppose that the ring were circular as *abcde*, Fig. 3, and that y_1 were given by (4). i would not be constant around the ring. Due to the drift w positive ions accumulate on the side b of the ring leaving a negative accumulation on side e. This gives rise to an electric field E' from the b to the e side of the ring. E' is in such a direction that, combined with H, it causes the charged particles of both signs to move at right angles to E' and H with a velocity $v' = E'\sin\phi/H$, where ϕ is the angle between E' and H. The movement together with the wabble of the earth's magnetic field (section 7) causes ions in or near the equatorial plane to move away from the sun roughly parallel to the equatorial plane. Thus ions and electrons formed in the region *bae*, Fig. 3, flow toward *ba'e*. If the ring has an angular width of 20° at $\theta = 90°$ then at *a'*, i.e. at $\theta = 0$, because of its greater proximity to the earth and its greater supply and less loss of ions than $\theta = 90°$, the ring may have an angular width of as much as 70°, in agreement with the observations of Barnard[3] and Newcomb.[4] Likewise ions and electrons formed at *bcde*, Fig. 3, stream toward *c''GFd''* maintaining their concentration in the equatorial plane, the motion being modified by radiation pressure after they get beyond 100,000 km (section 10). The flow or streaming of the ions away from the sun is a maximum at the equator and falls off rapidly at the higher latitudes. Therefore the details of the ion movements brought out here do not disturb the aurora theory[7] but offer helpful additions to the theory which will be considered in a future paper.

To work out E' and v' exactly throughout the region *BGFD*, Fig. 3, is intricate. Approximate calculations show that the ions and electrons stream away from *BcdD* about as rapidly as they are produced and that v' becomes less as z increases; beyond $z = 100{,}000$ km v' is negligible compared with the effects of radiation pressure. An average v' of order 1 km sec^{-1} from $z = 50{,}000$ km to 100,000 km is indicated.

10. *Radiation pressure causes the zodiacal ions and electrons to stream away in or near to the plane of the ecliptic.* The accelerations due to the pressure of solar radiation at the earth were estimated in section 9 to be 1.5, 5.2 and 20.8 cm·sec^{-2}, respectively, for a nitrogen, helium and hydrogen atomic ion; these are also the values of the earth's gravitational accelerations at about 210,000, 96,000 and 45,000 km, respectively. The solar gravitational attraction is just cancelled, or nearly so, by the centrifugal force due to the velocity of the earth in its orbit around the sun and may be neglected. Thus ions and electrons which are formed in the region *bcde*, Fig. 3, and which move out in

[31] Hulburt, Phys. Rev. **34**, 1167 (1929).

the equatorial plane with velocity v' find themselves subjected to a radiation pressure parallel to the ecliptic plane which beyond, say, $z = 100{,}000$ km is equal to or greater than the earth's gravitational attraction.

In order to find out what happens to these particles we must examine the motion of a neutral ion cloud of finite size in a magnetic field H acted on by a constant force F, F being normal to H. Take H along the X-axis and F along the Y-axis. Then the ions drift along the Z-axis with a velocity F/He, the positive and negative ions going in opposite directions. As a result of the drift a separation of charge occurs which causes an electric field E along Z in such a direction that, combined with H, it causes the ions of both signs to move in the direction of F with a velocity v. The energy acquired from F goes into the kinetic energy η of the ions and the energy ξ of the electric field. At all times $v = E/H$. $\eta = mv^2y/2$ and $\xi = E^2/8\pi c^2$. Therefore $\xi/\eta = 2H^2/8\pi c^2 my = 2.85H^2/y$. With H two or three orders of magnitude less than y, as in the present problem, ξ/η is less than 10^{-4}. Thus the energy taken by the field E is small compared to that of the moving ions. Therefore the ion cloud moves across the magnetic field under the action of the force approximately as it would if there were no magnetic field. This of course can not keep up indefinitely. For, as they recede from the earth the ions reach a region where the magnetic field is so small that the simple formulas used in the foregoing sentences become invalid. Actually the ion progresses along a cycloidal path and $v = E/H$ is approximately the average velocity of progression. The approximation breaks down when the radii ρ, equation 3, of the loops of the cycloid become comparable with the size of the ion cloud. This occurs at about $z = 500{,}000$ km for a radiation pressure acceleration $p = 5$ cm $\cdot$ sec^{-2} and an ion cloud 50,000 km across. At this distance the ions commence to progress away from the sun more slowly than they would if their acceleration were constantly 5 cm $\cdot$ sec^{-2}, their motion being in large cycloidal loops. At greater distances, beyond 10^6 km, the earth's magnetic field becomes inappreciable, the ion paths straighten out and the ions move away under light pressure.

We now make use of what has been said about the motion of the zodiacal ions and electrons and give some numerical calculations. Ions formed on the day side of the earth for the most part do not drift to the night side. For an ion at a or a', Fig. 3, hardly stays there more than 10^6 sec (section 7) before falling back to the earth; its drift velocity w is of the order 10^2 cm $\cdot$ sec^{-1}, and in 10^6 sec it drifts eastward only 1000 km, which does not take it very far around the ion ring. Therefore the ions on the night side of the earth practically all come from those formed in the region *bcde*, Fig. 3. Consider ions and electrons at b, Fig. 3, at winter solstice; these are at the intersection of the planes of the equator and the ecliptic. Due to the combined effects of a light pressure acceleration $p = 5$ cm $\cdot$ sec^{-2} in the ecliptic plane and an average velocity $v = 1$ cm $\cdot$ sec^{-1} in the equatorial plane out to $z = 100{,}000$ km, and zero beyond this (v' being due to E' which arises from the gravitational magnetic drift w, section 9) the ions move in 3×10^4 sec or 8.3 hr away from the sun to a position about 49,500 km from and 12,000 km south of the ecliptic. After

this v' becomes negligible and the accelerations which act on the ions are p and g, g being the acceleration of the earth's gravitational attraction. In the next 4×10^4 sec or 11.2 hr the ions move away from the sun to z about 400,000 km, at this distance having a velocity around 3 or 4 km·sec^{-1}. The component of the vector $p+g$ toward the line AK, Fig. 3, is about 0.5 cm·sec^{-2}, and thus the ions progress about 4000 km toward AK. The ions then continue to progress away from the sun with a lessened acceleration until z is perhaps 10^6 km, at the same time they bear in slightly closer to AK. After this the effect of the earth's magnetic field becomes inappreciable and the ions stream away with the full light pressure acceleration p. The earth's shadow has practically no effect on the motion, the ions in the shadow moving along with those in full sunlight. This is because the ions in the shadow are few compared with those in the sunlight, since the cross-section of the shadow is small compared with that of the ion cloud, and because the ions in the

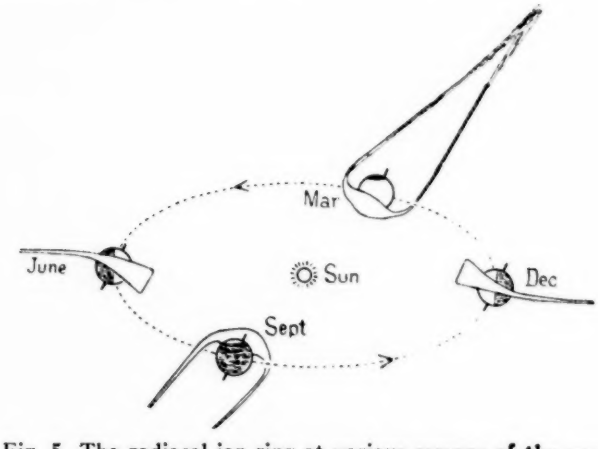

Fig. 5. The zodiacal ion ring at various seasons of the year.

sunlight move by setting up the electric field E, which acts equally on the sunlit and the dark ions.

11. *Comparison of the atmospheric theory of the zodiacal light with observation.* The results of the theory of the zodiacal ions worked out in sections 5 to 10 are represented in Fig. 5. The figure is not drawn to scale. On the daylight side of the earth the zodiacal ion ring is wide and follows the plane of the earth's equator. On the night side the ring is narrow, is warped off the equatorial plane roughly on to the ecliptic plane and trails off to a great distance. Referring to the portions of the zodiacal band at roughly $\theta=90°$ to 130° from the sun it is seen from Fig. 5 that both the morning and evening zodiacal cones should appear somewhat to the south of the ecliptic near winter solstice and to the north of the ecliptic near summer solstice. Around spring equinox the evening cone should be to the south and the morning cone to the north of the ecliptic, with a reversed position of the cones at autumn equinox. Fig. 6 gives a plot obtained from Jones' observations.[8] The ordinates are the positions in degrees to the north or south of the ecliptic of

the center of the zodiacal cone for $\theta = 90°$ to 130° at solstice and 70° to 130° at equinox, approximately; the dots and crosses refer to the evening and morning cones, respectively. The course of the dots and crosses is in accord with the theoretical deductions. The dots and crosses are together at the solstices, those at winter solstice being below those at summer solstice; the crosses are above the dots at spring equinox and below the dots at winter equinox. The observations of Cassini[8] made in 1685 to 1687 are plotted in Fig. 6, the circles being the evening observations and the triangles the morning observations. They agree well with those of Jones, as Jones himself remarked. The magnetic storms, shown by the vertical lines in Fig. 6, are discussed in section 13.

Although the march of the crosses and dots of Fig. 6 is in qualitative agreement with the present theory, there is a quantitative discrepancy. At equinox the morning and evening cones are separated in latitude by

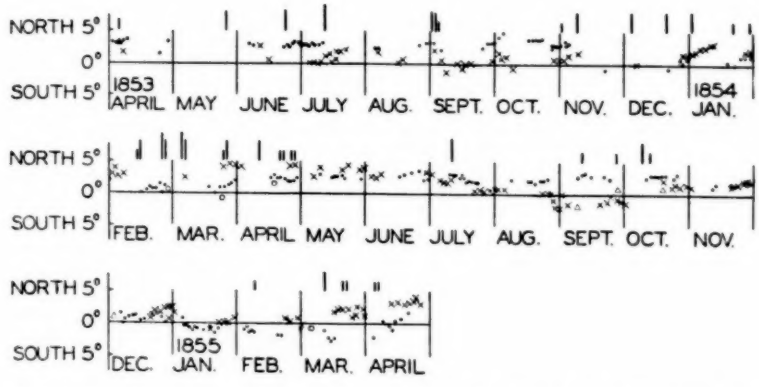

Fig. 6. Positions in degrees to the north or south of the ecliptic of the evening and morning zodiacal cones, shown by dots and crosses, respectively, from the observations of Jones. The observations of Cassini are shown by circles, evening, and triangles, morning.

about 5°, whereas if the cones lie partly along the earth's equatorial plane the separation should perhaps be greater than 5°, but not more than 46°. Whether the discrepancy is serious or whether it will disappear upon further attention to theory or observation can not be said at the present time. On the other hand the north and south shift of the cones of about 5° from winter to summer solstice agrees with the theory. If one plots from Jones' drawings the positions of the apexes of the zodiacal cones to the north or south of the ecliptic the points show the same general trend as those of Fig. 6, but much less pronounced and with many irregularities due no doubt to observational errors. The average deviation of the apexes from the ecliptic is less than 2°. This would be expected on the present view for the apexes of the cones are light from zodiacal ions which are probably more than 100,000 km away.

The dots and crosses of Fig. 6 are on the average about 2° to the north of the ecliptic, whereas one would expect the average over a year to be on the ecliptic. In explanation we follow a suggestion of others[9] and make use of

the fact that the atmospheric transmission due to haze, etc., decreases toward the horizon. Thus if the ecliptic and the zodiacal cones had a slant, say, to the south of the vertical with the horizon, an observer would place the zodiacal cones too far to the north. Any traces of twilight would accentuate the error, although Jones avoided errors from twilight by making most of his observations after the sun was 18° below the horizon. The correction due to the slant of the cones shifts the points of Fig. 6 generally southward and therefore is qualitatively in the right direction to bring their average close to the ecliptic, without however disturbing the equinox and solstice relations brought out in the last paragraph. In more detail, from April to December, 1854, the zodiacal cones slanted in general to the south; the points of Fig. 6 in this period should therefore all be shifted a degree or so southward. In January, 1855, the ecliptic was nearly vertical and the points need no correction. In February the correction is northward on both dots and crosses, in March is zero for the crosses and slightly northward for the dots, and in the latter part of April is southward again for all the points. Thus we find a simple explanation of the curious fact[1,2,9] that in general observers in northern and southern latitudes have recorded the zodiacal cones to the north and the south of the ecliptic, respectively. From the foregoing analysis of Jones' observations it seems that it is not the latitude of the observer but the slant of the cones with the horizon that is important.

From Fig. 5 one can see how Jones and other observers sometimes got an apparent negative parallax of the zodiacal cones. At equinox the observer found himself south of the ecliptic in, say, the evening. He recorded the position of the evening cone against the stars. By the rotation of the earth on its axis he was carried to the north of the ecliptic in the morning and recorded the position of the morning cone. Upon comparing the two results he found to his surprise that the zodiacal cone had apparently moved with him from the south to the north of the ecliptic. Thus the parallax came out zero or negative, which is to be expected on the present view because the evening and morning cones are two different portions of a warped zodiacal band.

From the observations of Serpieri, Heis, Weber and others (see reference 9) as well as from those of Jones it seems to be an accepted fact that the zodiacal cones are longer at solstice than at equinox. The present theory does not provide an explanation of this. Qualitatively, at any rate, it does not point with any clearness to marked seasonal variations in the shape of the cones. The theoretical calculations of the motions of the zodiacal ions have been pretty rough and it is possible that many details, and perhaps important ones, have escaped us.

12. *Moon zodiacal light.* Here we have to deal with conclusions so incomprehensible on any theory that we think they are in error. Nor are we the first to think this, for Newcomb[1] commented on Bayldon's[1] observations as follows, "He (Bayldon) also describes the moon as adding to the zodiacal light in her first and last quarters, a result so difficult to explain that it needs confirmation." To give a typical experiment; the observer an hour or two after sunset could see as usual the western zodiacal cone but ordinarily he

could not see the zodiacal band extending across the sky down to the eastern horizon. The moon was about to rise in the east and he thought that he could see the zodiacal band near the eastern horizon. He concluded that this was due to an illumination of the zodiacal particles by the moonlight. However, the intensity of moonlight at the earth is 10^{-6} of that of sunlight and the conclusion would be that the brilliance of the zodiacal cone or band which is barely discernable when illuminated by sunlight is perceptibly increased by light 1,000,000 times weaker. The moon zodiacal light observations were made when the moon was less than 10°, and usually less than 5°, below the horizon. Therefore moon twilight would certainly have interfered with the observations and perhaps moon twilight was all that the observer saw. Jones recorded 13 moon zodiacal light observations and by chance 8 of these were during magnetic storms when the zodiacal light might have been unusually brilliant, because of the solar activity and not because of the moon.

On the present theory the moon, being about 380,000 km from the earth, moves through the zodiacal ions in the region K, Fig. 3. At 10,000 km from the center of the moon the acceleration of the moon's gravitation is 5 cm sec^{-2}, which is comparable with the light pressure acceleration. Therefore the moon might sweep a hole through the zodiacal ions probably less than 20,000 km in diameter. The magnetic moment of the moon may be estimated[32] to be considerably less than 10^{-2} of that of the earth and the effect of the moon's magnetic field on the ions is probably inappreciable beyond 1000 km from the moon compared to that of light pressure. The hole in the zodiacal ions caused by the moon would be difficult to observe, being wrongly oriented to the terrestrial observer, and being healed quickly by the ion flow would not be expected to give rise to zodiacal or gegenschein variations which could be detected.

13. *Zodiacal light variations and solar outbursts.* The effects of sunlight in producing the zodiacal ions and in stimulating them to emit light, which have been described for a quiet sun, are accentuated during solar outbursts. According to the ultra-violet light theory[7] of aurorae and magnetic storms the solar outburst is a flare of ultra-violet light. The ultra-violet flare would in general be expected to increase the number of the zodiacal ions and the intensity of their fluorescence. We make no attempt here to enter into a complete discussion of the complicated effects which the flare might produce, but a few simple cases are of interest. The zodiacal ion ring on the day side of the earth might be compressed toward the earth because I_0 is increased and t is decreased during the flare (section 6). Therefore the portion of the ring from $\theta = 0$ to 90° might be widened during a magnetic disturbance. Apparently this is what happened during the latter part of June 1853 according to Jones' observations. The position and shape of the ring on the night side of the earth would not be expected to be greatly changed by the flare. In keeping with this idea the magnetic storms are shown by vertical lines in Fig. 6, and it is seen that the course of the dots and crosses is on the whole undisturbed during the magnetic storms.

[32] From equation (12), Gunn, Phys. Rev. **34**, 335 (1929).

A flickering of the intensity of the ultra-violet wave-lengths of the flare which cause the fluorescence of the zodiacal ions would cause pulsations in the entire body of the zodiacal light, as are observed. Various types of flares would be expected to occur (see the discussion of an earlier paper[33]), in particular, the ionizing wave-lengths might be feeble compared to the fluorescent wave-lengths. This might occur at any time or when the flare was warming up to storm intensity. In the first case there might be zodiacal light changes with no accompanying magnetic storm, and in the second case the zodiacal light variation would be followed by the magnetic storm. Instances of both these possibilities are found in the data of section 2. For example, the zodiacal light fluctuations of November 3, 1929, (section 2) were seen at about 3 A.M. and the magnetic storm began 4 hours later. Similarly, auroral displays and vagaries in the propagation of wireless waves are known[33] to occur before a magnetic storm at times. The Radio Division of this Laboratory has noticed on a few occasions that wireless communication was very unusual several days before a magnetic storm; the storm was actually predicted in advance, the feeling at the time being that the prediction was about as certain as a weather prediction.

14. *The gegenschein.* The ions which stream away from the region *bcde*, Fig. 3, form a sheet mainly in the ecliptic plane extending throughout the region *BGKFD*, which seen edge-on is the zodiacal band. The ion densities are somewhat greater near the boundaries *bc''* and *ed''* of the sheet than in the interior regions. As shown in section 10 the boundaries swing into some extent toward the line *AK*, and at about $z=0.5\times10^6$ km the ions progress more slowly away from the earth until $z=10^6$ km is reached, whereupon they stream away with the full light pressure acceleration like the particles of a comet's tail. Thus looking end-on at the ion stream the terrestrial observer sees it as a patch of greater luminosity on the zodiacal band. This is the gegenschein. If the cross-section of the stream were 100,000 km in width along the ecliptic and 40,000 km high and if the equivalent optical distance were 10^6 km, the patch would be 6° wide along the ecliptic and 3° high, as seen from the earth, and its parallax as determined by two observers 20,000 km apart would be 1°. These values agree with observation[5,6]; Barnard[5] stated that the brighter portion of the gegenschein is about 7° in diameter fading insensibly into the night, the luminosity sometimes being perceptible to a diameter of more than 30°. The present theory of the gegenschein is of course quite different from the meteorite theory of Gyldèn and of Moulton.[34]

That the gegenschein may be a comet tail appendage of the terrestrial atmosphere was mentioned long ago by Arrhenius, Evershed and others.[1] Barnard[5] suggested that the atmosphere surrounding the earth acts as a lens to give a concentration of light somewhere along the line *AK*, Fig. 3. This would make a spot of illumination if there were particles there to be illuminated. Exact calculations are difficult but approximate ones show that the con-

[33] Hulburt, Phys. Rev. **34**, 344 (1929).

[34] Moulton, "Celestial Mechanics," page 305 (1914).

centration of the light due to the lens, or refraction, effects probably occurs beyond $z=0.5\times10^6$ km and that the concentration is not very great, perhaps about the same as the effects of diffraction. The apex of the cone of the earth's geometrical shadow is at $z=1.37\times10^6$ km.

The present theory gives no clear indication of marked seasonal variations in the appearance of the gegenschein, but Barnard[5] found that the gegenschein "undergoes singular changes in form and that these changes are periodic with the seasons." To explain Barnard's observations we turn to the magnetic storms. In a time of solar quiescence the gegenschein would be a small spot elongated into the zodiacal band along the ecliptic. During a magnetic storm the spot would be larger for the number of gegenschein ions and their fluorescent light would be increased. From 73 observations extending over 15 years Barnard concluded that the gegenschein was large and round in February, March (especially in the latter part of the month), April, August, September, the first part of October, and November. It was small and elongated along the ecliptic in January, July and the latter part of October. The milky way interfered with observations in June and December, and there were few observations in May. These facts are pictured in Fig. 7.

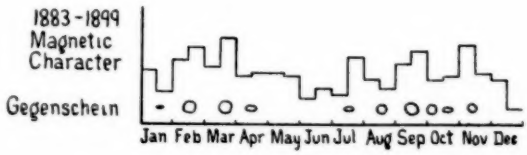

Fig. 7. Average magnetic character curve and Barnard's observations of the gegenschein for the years from October 1882 to February 1899.

Barnard made the 73 observations of the gegenschein from October 1883 to February 1899. We have added together all the magnetic storms for the first and last halves of each month throughout this period and have plotted the results in the broken curve of Fig. 7. In the addition storms of intensity 1, 2, 3 and 4 counted as 1, 2, 3 and 4, respectively. The curve is a magnetic character curve for the 15 years. It is seen that very roughly the gegenschein was large during epochs of magnetic storms and small during magnetic calm. The magnetic character curve has an ill defined maximum near equinox and a minimum near solstice, and thus has a sort of seasonal period. Fig. 7 can not be regarded as offering convincing evidence of a connection between magnetic storms and changes in the gegenschein. Further evidence would be desirable. It suggests, however, that the seasonal variations in the gegenschein were perhaps due to solar disturbances rather than to the tilt of the earth's axis.

15. *The rate of escape of the earth's atmosphere.* Zodiacal ions and electrons in the region *BDFG*, Fig. 3, which get beyond roughly 100,000 km move away under the solar radiation pressure. They do not come back to the earth. The zodiacal light and the gegenschein are the last fleeting evidences of particles which are leaving the earth never to return. If 1/10 of the high flying atoms

and molecules pass into space *via* the zodiacal band and the gegenschein, there is a loss of 10^6 particles $\cdot$ cm^{-2} $\cdot$ sec^{-1} from the atmosphere, or 10^{-6} of the entire atmosphere in 10^6 years. This is, if anything, an under-estimate, but a rate of escape of this amount, or even two or three orders of magnitude greater, seems small and open to no objection on general cosmogonical grounds.

We may go a step farther. Geophysicists[35] have found a difficulty in explaining the smallness of the amount of helium, 10^{13} atoms in a 1 cm^2 column, present in the earth's atmosphere. They estimate that the average acid rock sets free helium at the rate of 10^7 atoms of helium per year per gram of rock, and therefore that, say, 100 grams of acid rock per cm^2 would in 10,000 years produce the 10^{13} helium atoms. Thus in the long periods of geological time much more helium would be produced than is found to exist, especially so since no processes are recognized which would remove the helium by absorption back into the crust of the earth. The present theory points a way out of the difficulty in that it suggests that helium may escape from the atmosphere more rapidly than the other gases. For helium atoms, being lighter, will be sprayed away from the earth with greater velocities than the heavier nitrogen or oxygen molecules and atoms. More energy is required to ionize helium than the other gases and hence the helium particles reach much greater distances from the earth before being ionized and swept away by radiation pressure. Therefore, compared with oxygen or nitrogen ions, few of the fast flying helium ions return to the earth, and the rate of escape of the helium into space may be of the same order of magnitude as the rate of supply from the earth.

[35] Holmes, Geological Mag. **2**, 60 (1915), and references given in Jeffreys, "The Earth."

POLAR MOLECULES, THEIR CONTRIBUTION TO ENERGY LOSS IN DIELECTRICS

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(Received March 8, 1930)

Abstract

Recently suggestion has been made that even at frequencies as low as those of commercial power circuits the theory of molecular orientation may serve as an explanation of at least a portion of the dielectric energy loss. This paper is an attempt to examine this suggestion on the basis of the Debye theory and the available experimental data. It reaches the following conclusions:

(a) The contribution of molecular orientation to the energy loss at frequencies below ten thousand cycles per second is negligible at the temperatures of zero and ten degrees Centigrade, for glycerine.

(b) For temperatures higher than ten degrees the contribution becomes still smaller and in all probability vanishes.

(c) The probability that any substantial portion of the normal dielectric loss found in the usual insulating oils, at commercial frequencies, may be accounted for on the basis of the Debye theory, is remote.

(d) In order to determine the effect of the dipoles in their contribution to dielectric loss, very accurate determinations of the dielectric constant must be made, especially for those substances that show small changes in dielectric constant with temperature and frequency.

Introduction

THE principle interest in Debye's theory of polar molecules has centered in its explanation of hitherto anomalous behavior of dielectric constant as related to temperature and frequency, and in the light it has thrown on the groupings within the molecules of compounds and mixtures. Little attention has been given to the necessary energy dissipation associated with the oscillation of polar molecules in an electric field. These losses, in absolute energy values, are relatively unimportant within the luminous range of frequencies although their close interrelation with absorption and anomalous dispersion is well understood. Under certain conditions, however, it is to be expected that an energy maximum will be encountered at some lower frequency. In general these maxima should occur at frequencies which are still relatively high, as related to those pertaining to the electric systems of practice, with the possible exception of those of radio transmission. There is in fact an increasing tendency in the literature of dielectric loss to invoke the frictional oscillation of the Debye polar molecule in explanation of the loss phenomenon. There is some evidence that this may be true, in part at least, within the upper range of radio frequencies. Some authors [1,2] however

[1] D. W. Kitchin, Trans. A. I. E. E. **48,** April (1929).

[2] D. W. Kitchin, and Hans Müller, Phys. Rev. **32,** 979 (1928).

have attempted to extend the application of the theory, in the matter of energy loss, even to the low alternating frequencies of commercial power circuits. This paper is an effort to examine this last proposal from the standpoint of the theory and the available experimental data. It reaches the conclusion that there is little probability that in any of the materials as commonly used for insulation, any appreciable part of the observed dielectric loss is to be accounted for by the oscillation of polar molecules.

In his discussion of anomalous dispersion and absorption Debye[3] considers the effects of dipole oscillation in periodic electric fields. He develops the distribution function of the moments and shows that the mean moment of the molecules is a complex number. The meaning of the complex moment is that there is a difference in phase between the moment and the external force. This difference in phase between the field intensity and polarization is accompanied by energy absorption. Since the moment is complex the molar polarization and hence the dielectric constant are complex. The dielectric constant must therefore be of the form

$$\epsilon = \epsilon' - j\epsilon''.$$

This means that in a dielectric under alternating stress, instead of having a current that is 90 degrees ahead of the voltage in phase, we also have a component of current which is in phase with the electromotive force and therefore causes an energy loss. The constant ϵ' is the 90 degree component and is the value that is usually determined by ordinary bridge methods. Considering a condenser in an electric circuit, Debye shows that $\epsilon' = C/C_0$, where C_0 is the capacity of an empty condenser and C is the capacity of the same condenser with a dielectric. The in-phase or loss component is ϵ'' where $\epsilon'' = 1/\omega W C_0$ and we consider the condenser in question as having no losses and having a capacity C shunted by a resistance W. The energy loss may therefore be expressed in terms of the phase defect angle Φ so that $\tan \Phi = \epsilon''/\epsilon'$.

It is natural to expect that under the influence of a periodic electric field the polarized molecules will tend to oscillate following the direction of the field. In a liquid dielectric this rotational motion would take place in a more or less viscous medium and the motion of the dipoles through this medium would be opposed by friction and so lag in phase behind that of the field. Heat would be generated which we observe as energy loss. This energy loss is that which would contribute the phase defect angle mentioned above.

Bearing in mind that the polar oscillation takes place during the period of free motion of kinetic agitation, we must conclude that the variations and losses in question would generally be associated only with frequencies relatively high. The theory however has recently been invoked by Kitchin and Müller to explain the phenomena observed in low frequency fields. Kitchin suggests in fact that the orientation of the molecules in a field of frequency as low as 60 cycles per second may account for at least a portion of the observed energy loss. From the relation of the time interval of molecular orientation with the kinetic activity it would appear that the orientation in a low fre-

[3] P. Debye, Polar Molecules, The Chemical Catalog Company, 1929.

quency field would be such that there would be no phase difference between the field intensity and the polarization and hence no energy absorption.

Method of Attack

As mentioned above the energy loss can be expressed in terms of the phase defect angle, that is,

$$\tan \Phi = \epsilon''/\epsilon'$$

Debye derives the following expressions for ϵ' and ϵ'';

$$\epsilon' = \epsilon_0 + \frac{\epsilon_1 - \epsilon_0}{1 + [(\epsilon_1 + 2)^2/(\epsilon_0 + 2)^2]\omega^2\tau^2}$$

$$\epsilon'' = (\epsilon_1 - \epsilon_0)\frac{[(\epsilon_1 + 2)/(\epsilon_0 + 2)]\omega\tau}{1 + [(\epsilon_1 + 2)^2/(\epsilon_0 + 2)^2]\omega^2\tau^2}.$$

In these equations the values ϵ_0, ϵ_1 and τ are constants for a given material at a given temperature, the value of ω is 2π times the frequency. The quantity τ is known as the relaxation time of the liquid and is the time required for all the molecules to revert to a random state after the removal of the impressed field. The dielectric constant ϵ_0 is the dielectric constant at very high frequency and the constant ϵ_1 is the dielectric constant for zero frequency. It is readily seen that if the constants ϵ_0, ϵ_1 and τ are known it is possible to calculate from the above two equations the values of ϵ' and ϵ'', and hence the phase defect angle, for any frequency.

Table I.

Temp. °C	Frequency Cycles/sec.	ϵ_1	ϵ_0	$\tau \times 10^9$	Normal pf	Power Factor due to dipole	% Normal pf due to dipole
			Glycerine				
0	60	37.38	6.72	1.28	0.0566	0.00000175	0.0031
0	100	"	"	"	0.0939	0.00000298	0.0032
0	1000	"	"	"	0.6866	0.0000298	0.0043
0	10^4	"	"	"	0.9944	0.000298	0.030
0	10^5	"	"	"	0.9999	0.00298	0.298
0	10^6	"	"	"	1.0000	0.0298	2.98
0	6×10^6	"	"	"	1.0000	0.1742	17.42
0	3.15×10^7	"	"	"	1.0000	0.6051	60.51
0	9.74×10^7	"	"	"	1.0000	0.6667	66.67
10	60	44.51	5.22	47.3	0.0297	0.000001	0.00337
10	100	"	"	"	0.0492	0.00000169	0.00343
10	1000	"	"	"	0.4432	0.0000169	0.00381
10	10^4	"	"	"	0.9802	0.000169	0.0172
10	10^5	"	"	"	0.9998	0.00169	0.169
10	10^6	"	"	"	1.0000	0.01689	1.69
10	10^7	"	"	"	1.0000	0.1659	16.59
10	10^8	"	"	"	1.0000	0.7646	76.46
			n-Propyl alcohol				
−60	60	32.79	2.747	2.46	—	0.00625	
−60	6.0×10^6	"	"	"	—	0.5028	
−60	3.16×10^7	"	"	"	—	0.7443	
−60	9.74×10^7	"	"	"	—	0.4751	

It should be possible to determine these three constants by measuring ϵ' for three different values of ω and solving three simultaneous equations. Therefore from data taken at three frequencies it is possible to calculate, for any frequency, the contribution of molecular orientation to the energy loss in a dielectric. We can therefore show the importance or lack of importance of such a contribution at low frequency.

A search of the literature in an effort to find data that would permit such calculations to be carried out revealed only a meagre amount of suitable material. The data from which the calculations, given below, were made were taken from the work of Mizushima.[4] On the basis of his observations on glycerine the calculations shown in Table I were made. The table gives the energy loss in terms of power factor.

Results of Calculations

The column headed "normal power factor" was calculated as a basis for comparison. This is the power factor due to dielectric constant and resistivity and is approximately the value that would be obtained by the usual bridge measurements at low frequency. The calculation was made on the basis of the following formula,

$$\tan \theta = (18 \times 10^{11})/(f\epsilon'\rho)$$

In this formula θ is the phase angle, f is the frequency in cycles per second, ϵ' is the dielectric constant and ρ is the resistivity in ohms per cm^3.

The results show that for glycerine the dipole contribution to the energy absorbtion is negligible for frequencies below ten thousand cycles, both for zero and ten degrees Centigrade. Furthermore, at the low frequency of 60 cycles per second their contribution is only three thousandths of one percent, a quantity entirely out of the range of accuracy of ordinary loss measurements. These results are strikingly brought out in Figure 1 where the value of power factor, for glycerine, is plotted against frequency. From Mizushima's data it is immediately apparent that for temperatures above ten degrees Centigrade the effect of the orientation becomes still smaller and certainly vanishes for low frequency.

Table I also gives some results on n-propyl alcohol and shows the small value of the power factor for 60 cycles compared to the high frequency value. The data are for -60°C and no resistivity values being available for this temperature, it was not possible to calculate the "normal power factor." However, it would appear that for temperatures near that of room, where the viscosity of the alcohol would be considerably less than at -60°C, the loss would be considerably less and would probably disappear for 60 cycles.

The paper by Kitchin[1] gives curves of dielectric constant and power factor against temperature for wood resin. The curves given are for 10^7, 10^6 and 60 cycles per second and the suggestion was made on the basis of these curves and the curves of viscosity and dielectric loss for the same material. It would appear that these three measurements should permit calculation of the dipole

[4] San-ichiro Mizushima, Bull. Chem. Soc. Japan **1**, 47, 83, 115, 143, 163 (1928).

contribution. Such a calculation was attempted but was not satisfactory, since the observed changes in dielectric constant were too small. The calculations depend on differences in the value of the dielectric constant and it is thus evident that accurate determinations of that quantity are essential. Furthermore, it was necessary to take the data from the published curves which are not reproduced with sufficient fidelity. This was apparent from the fact that the same curves published in two different papers[1,2] were not in entire agreement.

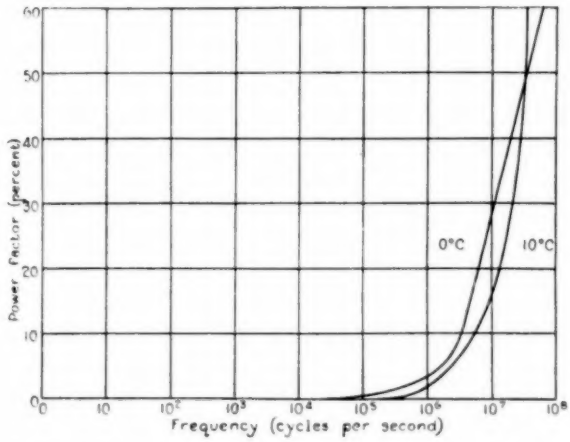

Fig. 1. Power factor due to molecular orientation. Glycerine at 0°C and 10° C. (Calculated curve.)

The "normal power factor" calculated as indicated above is probably somewhat smaller than that which would actually be measured since the calculation made on this basis takes no account of energy loss due to the "absorption" that is observed in short time studies of dielectrics. A recent paper by Whitehead[5] shows beyond doubt that dielectric absorbtion in certain cases accounts for at least 95 percent of the dielectric loss. Taking this property into account, the dipole contribution would be even smaller than indicated in the last column of Table I, where the dipole contribution is given in percent of the "normal power factor."

Effects in Insulating Oils

The suggestion of Kitchin, that the phenomenon of molecular orientation might account for energy absorbtion at 60 cycles was made with the idea of applying the theory to dielectrics used in commercial insulation. No other data in connection with such insulation are available from which calculations, similar to those made for glycerine, could be made.

So far as the commercial insulating oils are concerned there are certain general facts that enable us to estimate the possible effects of dipole orientation. It is obvious that in order to apply the theory to any liquid dielectric

[5] J. B. Whitehead, Jour. Frank. Inst. **208,** No. 4, October (1929).

the liquid must first of all be polar, that is, possess an electric moment. Probably the most used insulating oil is the well-known "transil" or transformer oil. This oil is a straight chain hydrocarbon and certainly possesses very small polarity, if it has any at all. It is certain that for this particular material dipole orientation plays no part in the energy loss.

As for the other insulating oils, particularly those used in high voltage impregnated paper cables, the lack of fundamental knowledge as to their molecular structure makes it impossible to estimate with any degree of precision the possible effects of orientation. The fact that the dielectric constant of this type of oil is always small, in the range of from say 2 to 3, and the dielectric constant of materials of the nature of glycerine is from ten to twenty times as large indicates that the effect of molecular orientation must necessarily be considerably smaller in such oils than in glycerine. And as we have shown the energy loss due to molecular orientation, at low frequency, is negligible for glycerine; it would seem safe to assume therefore that it should certainly be negligible for the insulting oils.

The author wishes to express his appreciation to Dr. J. B. Whitehead and to Dr. K. F. Herzfeld for their helpful suggestions during the preparation of this paper.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Possibility of Determining the Energy of the Cosmic β-Particles by Magnetic Deflection

In a recent letter to this section, Tuve[1] has pointed out how the scope of the Bothe and Kolhörster[2] coincidence method of investigating high-velocity β-particles can be greatly enlarged by making use of multiple coincidences in three of more electron-counting-tubes instead of the usual method of counting coincidences in only two counters. As Tuve has shown, there are two important advantages in this method: (1) a pair of counters can be used to define a beam of β-particles which is subsequently picked up by a third counter after being scattered, deflected by a magnetic field or otherwise experimented upon, and (2) the number of multiple coincidences occurring by chance can be reduced to a much smaller fraction of the true coincidences, making it possible to work with a beam of much smaller angle than can be used with only two counters.

When Tuve's note appeared, the writer had begun an experiment based on exactly these considerations in an attempt to obtain further information on the nature of the cosmic β-particles discovered by Skobelzyn[3] and investigated by Bothe and Kolhörster.[2] It is planned to attempt a magnetic deflection of these particles, for such an experiment would test the possibility that they may be protons as well asgive a direct measure of their energy. Definite knowledge of their energy distribution would be of assistance in deciding whether these particles are the actual cosmic rays or are of a secondary nature.

It may be of interest to describe an experimental arrangement, (at present under construction), by means of which it appears feasible to measure the energy of β-particles (or protons) having energy up to the value of 10^9 electron-volts which these particles are estimated to have. A pair of Geiger-Müller[4] tube-counters will be used to "collimate" a beam of the particles, which are then passed through a region of strong magnetic field and are finally detected by a third counter placed at a suitable distance. By counting the number of particles which produce a triple coincidence in passing through all three counters, and by arranging the third counter to be suitably movable with respect to the axis of the apparatus, it will be possible to measure the deflection of the beam if sufficient deflection can be obtained. Calculation shows that with counting tubes of sufficient area and subtending a large enough solid angle to keep the intensity high enough to be measurable, a very strong magnetic field is necessary. Furthermore, on account of the necessity of using large counters, (our present "collimating" tubes are 4.4 cm in diameter and 27 cm long), this field must be produced over a considerable volume. These difficulties may be overcome by a device suggested by Skobelzyn,[3] who points out that magnetic deflection of particles of such enormous penetrating power can be produced by passing them directly through a magnetized iron bar. By this method it will be possible to produce a magnetic induction of about 20,000 over a sufficient volume. The loss of energy of the rays in passing through the 15 cm of iron which will be used is not serious since particles of 10^9 e-volts energy can be expected to experience a loss of only about 12 percent.

[1] M. A. Tuve, Phys. Rev. **35**, 651, (1930).

[2] W. Bothe and W. Kolhörster, Zeits. f. Physik **56**, 751, (1929).

[3] D. Skobelzyn, Zeits. f. Physik **54**, 686, (1929).

[4] H. Geiger and W. Müller, Phys. Zeits. **29**, 839, (1928).

A widening of the beam due to straggling in the iron is estimated to be negligible for particles of such high energy. Calculation shows that by choice of suitable geometrical conditions and under the assumption of a magnetic induction of 20,000 over a 15 cm path a deflection equal to the width of the beam (about 8 cm) can be obtained for β-particles with the assumed energy of 10^9 e-volts. A somewhat smaller but still detectable deflection can be expected for protons of the same energy. Intensity considerations indicate that under these conditions the number of true triple coincidences will be sufficient to be measurable by a few hours of registration and that the number of such coincidences occurring by chance can be reduced to a small fraction of the true ones.

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Houston, Texas,
April 2, 1930.

Magnetic Moment of the Sulfur Molecule

It is perhaps an open question as to whether the oxygen molecule is singly or doubly bound. According to Heitler and London the $^3\Sigma$ state indicates a singly bound molecule but Heitler and Herzberg have suggested that the second valence may reside in the exchange degeneracy of the electron orbits without involving the spins.

In the case of the sulfur molecule S_2 the evidence is more definite. Sulfur does not often form double bonds, and the fact that sulfur is a solid at ordinary temperatures and even in the vapor state is largely polymerized, indicates that the S_2 molecule is highly unsaturated. A $^3\Sigma$ state is to be expected.

The magnetic moment of the S^2 molecule has been determined in this laboratory and the prediction is confirmed. Since most of the S_2 molecules are in states of high rotational energy it would not be expected that the field would break the coupling between the spins and the rotational axis. Under these circumstances only a widening of the molecular beam in the inhomogeneous field would occur and this result has been obtained in the experiments. In some cases however a faint satellite line on the side of the broadened central image has been observed. This line is on the side next the knife edge where the field is strongest. It seems probable that the field is strong enough here to uncouple the spins from the rotational axis in those mole cules in the lower rotational states. If this is the case then the line is one of the three to be expected from a $^3\Sigma$ molecule with strong field quantization.

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Raman Spectra from Sulfur Dioxide

In view of the increasing interest which is being shown in the spectra of polyatomic molecules, we desire to report the results of some Raman effect measurements on sulfur dioxide. The material used was taken from a commercial tank; it was passed over phosphorus pentoxide to dry it and then condensed in a heavy walled Pyrex glass tube 2 cm in diameter and 20 cm long. During the condensation care was taken to exclude moisture; but no further purification than drying was considered necessary since the commercial product is ordinarily much better than 99 percent pure. When this glass tube was nearly filled with liquid, it was sealed off and subsequently used for the light-scattering experiments.

The Raman spectra were obtained with a mercury arc and the plates calibrated with

TABLE I. *Scattered lines from liquid* SO_2.

Frequency of modified line	Intensity	Frequency of exciting line	Frequency shift
24182.5	v.f.(diffuse)	24705.5	523.0
23560.4	st.	24705.5	1145.1
23371.2*	med.	24516.1	1144.9
23366.1*	weak (diff.)	24705.5	1339.4
22412.5	weak (diff.)	22938.1	525.6
21893.7	v.f.	23039.1	1145.4
21847.8	f.	22995.3	1147.5
21791.4	v.st.	22938.1	1146.7
21597.4	med. (diff.)	22938.1	1340.7

* These two lines overlapped on the plates; separate measurement was attempted since one line was much sharper than the other.

an iron arc. The apparatus and method of measurements were substantially the same as previously used in the case of liquid ammonia (Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929)). The results of the measurements are given in Table I. The frequencies of modified lines in cm^{-1}, given in the first column, are averages obtained from several plates. Reduction of the calibrating wave-lengths to vacuo has been made.

These modified lines show the existence of three shifts with the following average values; 524.3 cm^{-1}, weak (diffuse); 1145.9 cm^{-1}, strong; 1340.1 cm^{-1}, medium (diffuse). The last two of these shifts agree, within the limits of error, with the frequencies of the two strongest absorptions by gaseous sulfur dioxide found by Coblentz (Carnegie Institute Publication, No. 35, p. 177) in the infrared. The smallest shift lies outside of the range of Coblentz's measurements. It is of interest to recall that such direct agreement between Raman shift and infrared absorption frequency has not been found in the cases of carbon dioxide and carbon disulfide whose molecules have points of similarity with those of sulfur dioxide.

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S. STEWART WEST

Gates Chemical Laboratory,
California Institute of Technology,
March 31, 1930.

On the Reason for Pauli's Exclusion Principle

It is generally recognized nowadays that physics deals primarily with one aspect of human experience; thus has the philosophical contention of Berkeley and Kant become after a century one of the presuppositions of our science. It was substantially this principle that led Heisenberg, first to his quantum mechanics, and then to the Indetermination Principle.

An interesting attempt has been made by Condon and Mack (Phys. Rev. **35**, 579, 1930) to find in the same principle the ground for Pauli's exclusion rule. It is suggested that human beings are themselves in an antisymmetric quantum state and that for this reason we can perceive only those material structures which are likewise in an antisymmetric state; hence, for us, the apparent validity of the exclusion rule. By implication there may exist all round us another set of physical systems in non-antisymmetric states without our being able to perceive them at all; presumably (if I understand correctly) there may also exist another race of humans who are experimenting upon those other systems but who, not being quantum-mechanically antisymmetric, can no more perceive us than we can perceive them.

An adequate proof seems to be lacking, however, that such possibilities are actually contained in quantum mechanics; certainly they are not among the familiar results of the theory. If, for example, an "antisymmetric" atom were to encounter a "symmetric" one under a law of interaction that is symmetrical in the electrons of each, then it follows from "resonance" theory that the first atom could never bump the second one into an antisymmetric state, nor could the second bump the first into a symmetric state; each atom would retain its initial character. There is, however, no indication that each would simply pass by as if the other were not there at all. The photons emitted by symmetric atoms would also, on current theory, be indistinguishable from photons of the same size emitted by other atoms and so should be observable. Since the same considerations hold for systems of any size, no reason is apparent why an antisymmetric physicist should be unable to perceive at all a symmetric world, or, perceiving it, to form an antisymmetric (?) concept of its symmetry.

The same consideration seems applicable at first sight to Condon and Mack's alternative suggestion that the non-antisymmetric electrons may all have vanished from our ken into Dirac states of negative energy, which for such electrons form a set having no "bottom." It remains to be shown that the endless dropping of these electrons into ever greater depths of the abyss would have no effect upon our instruments. Perhaps they are physically imperceptible just as an electron or photon with infinite positive energy has a zero coefficient of absorption and so is physically non-existent. I hope the authors of the paper will give us an exact mathematical analysis of this point.

E. H. KENNARD

Department of Physics,
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April 4, 1930.

Influence of Accelerating Fields on the Photoelectric and Thermionic Work Function of Composite Surfaces.

With an accelerating potential of 22.5 volts, Ives and Olpin (Phys. Rev. **34**, 117, (1929)) found that the long wave-length limit of an alkali metal film on platinum progressed toward the red as the film thickness increased, reached a maximum and then receded when the film was made very thick. Experiments by the writer with a twenty volt accelerating potential confirm this result with the exception that the long wave-length limits observed were more than 1000 Angstrom units farther into the infra-red than those reported by Ives and Olpin. Although there is an optimum film thickness, as pointed out above, when an accelerating field is applied, such is not the case at *zero field*. Lowering the accelerating field causes the optimum thickness to increase until at zero field the long wave-length limit has been observed to change progressively from that of the background metal to that of the alkali metal *without a maximum excursion* and regression.

This investigation has also been carried over into the field of thermionics using a type *T* thoriated tungsten filament with a small carbon content. With an activation temperature of 1920°K, a test temperature of 1230°K and a test accelerating potential of 20 volts, the thermionic current increased to a maximum of 98×10^{-6} amp. per cm² at the end of 90 minutes activation. This time of activation had produced the optimum thickness. With continued activation the thermionic current decreased until at 280 minutes an equilibrium condition was produced with a current of 59.3×10^{-6} amp. per cm². This observation is thus exactly analogous to that reported for the photo-electric effect. Judging by abstract 62 of the forthcoming meeting at Washington this phenomenon has also been observed by W. H. Brattain who deposited the thorium on tungsten from an external source but made no mention of the importance of the accelerating field. In order to prove that an excess film thickness had caused the decrease in emission described above, the activation temperature was raised and the emission was observed to *increase* with time of activation reaching new equilibrium values for each temperature. At a temperature of 2085°K the rates of evaporation and diffusion were so balanced as to keep the surface covered to just the optimum thickness for maximum thermionic emission which was 98×10^{-6} amp. per cm². Further increase in temperature reduced the thermionic emission indicating that the equilibrium condition of the surface corresponded to a film thickness less than the optimum. Tests with *lower* accelerating potentials showed that the optimum thickness depended on the test potential and moved toward thicker films as the potential was decreased until at practically zero field the maximum emission of 40.5×10^{-6} amp. per cm² was attained after 200 minutes of activation at 1920°K and practically no decrease in emission was produced by continued activation. These experiments, showing such close relationships between the thermionic and photoelectric behaviour of thin films, lend support to the theory that the "thermionic" and "photoelectric" electrons in these experiments come from the same family, presumably the "free" electrons.

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April 17, 1930.

Capture of Electrons by Alpha-Particles

The important experiments of A. H. Barnes on the above subject reported in the Phys. Rev. for Feb. 1, 1930, render rather interesting the theory of x-ray emission independent of temporary excitation suggested in a recent letter of the writer's in the Phys. Rev., since the latter gives a very simple explanation of the dependence of electron capture on the relative velocity; the result of those experiments.

According to the theory, if the relative velocity is such that relative kinetic energy is $E=h\nu_n$ corresponding to a natural frequency of the alpha-particle, then there is a probability that the electron will penetrate to the *n*-level, radiate the energy $h\nu_n$ and emerge from the field of the nucleus with a zero relative velocity; the probability of capture is thus equal to that when the initial relative velocity is zero. On the other hand if the

initial relative velocity is not one of the critical values the electron will penetrate to a level n such that $h\nu_n$ is less than the relative kinetic energy, and finally emerge with a finite relative velocity, thus reducing the probability of capture.

On this theory therefore we should expect the energy to be radiated in two separate and independent frequencies, one being governed by the relative velocity of the electron and the alpha-particle, and the other by the probability laws pertaining to the capture of stray electrons.

Further, if this suggestion is true, we should expect that when the relative energy was not a critical value, then there should appear a finite percentage of electrons with a velocity nearly, but not quite, equal to the velocity of the alpha-particles, and independent of the initial velocity of the electron beam, or nearly so. This point could be tested by the first experimental tube of A. H. Barnes, using a magnetic separation of the various particles in the beam emerging from the collision region.

WILLIAM BAND

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March 15, 1930.

X-Ray Emission Independent of Temporary Excitation

The usual explanation of Kramer's rule is that only when an incident electron has an incident minimum energy $eV=h\nu_x$ is it able to remove an electron from the X level of an atom; in the subsequent refilling of the level the X-radiation is emitted. Kramers in particular has studied the results of this assumption, and has explained to some extent the intensity distribution of the continuous spectrum by means of the statistics of collision between free electrons and temporarily ionized atoms.

But may we point out that an electron is given, over and above any initial energy, sufficient extra kinetic energy due to the attraction of the nucleus, to remove the X electron at a head-on collision. If the electron impacts are perfectly elastic, then their masses being equal they merely interchange velocity, and the ejected electron eventually emerges with an energy equal to the initial energy of the incident electron. No radiation is emitted. If the impact is not perfectly elastic, then the ejected electron emerges with less energy, and the incident electron, instead of remaining in the X orbit, may be carried out to a level n where $ev>h\nu_n$, and radiation of frequency $\nu_x-\nu_n$ will be emitted when it drops back into the vacant X level. Both these processes can occur even when the energy $eV<h\nu_x$, contrary to experimental data.

To avoid this dilemma I would propose the following hypothesis. That an incident electron cannot penetrate to the n level of an atom unless (a) that level is vacant, or failing this, (b) the electron has sufficient initial energy $eV=h\nu_n$ to carry it out again into free space after radiating the energy $h\nu_n$ appropriate to the n level. That this energy is automatically emitted whenever an electron penetrates to that level, but that it may be emitted either in the fundamental frequency ν_n or else as a spectrum of frequencies $(\nu_n-\nu_{n+k})$, $(\nu_{n+k}-\nu_{n+k+l})$, etc.

The initial energy of the incident electrons is thus itself directly changed into radiation, and no temporary excitation of the atom is required.

It seems that the experimental facts force us to this position, but although it is an interesting move back towards the classical theory, it is nevertheless obvious that the wave mechanics will be required to give it a satisfactory theoretical basis.

WILLIAM BAND

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March 10, 1930.

Motion of Positive Ions through Gases

In a previous paper[1] the writer published the results of some experiments on slow moving heavy alkali ions passing through light gases at low pressures. The method used is that of Dempster.[2] The ions pass through a slit into the space 3 mm wide between the pole pieces of a magnet. The ions move in the magnetic field in a semi-circular path, passing out through a second slit into a faraday chamber, where they give up their charge to an

[1] R. B. Kennard, Phys. Rev. **31**, 423 (1928).

[2] A. J. Dempster, Phys. Rev. **11**, 316 (1918) et seq.

electrometer. From the curves showing the change in electrometer current with changing gas pressure and magnetic field, conclusions were drawn concerning the mean free path, neutralization, scattering, and loss of velocity of the ions in passing through the gas in the system.

Cox[3] using the same method with lithium ions passing through mercury gas, questions the possibility of distinguishing between scattering and neutralization. He assumes that the number of ions scattered along the slot between the pole pieces would be negligible compared to the number scattered into the pole pieces and so lost. Scattering would therefore have the same effect as neutralization; that is, at the higher gas pressures there would be a decrease in the peaks of the curves obtained, without a broadening of the base of the curves to both sides. This assumption is valid in the case of light ions in a heavy gas, but it is not necessarily valid for a heavy ion passing through a light gas. In fact a study, based on the kinetic theory, of the space distribution of the once-scattered ions, shows that scattering should have been observed in three of the four cases investigated by the writer.

Cox assumes that in a collision between an ion and a gas atom, the ion rebounds from the atom as from an immovable sphere. This is a legitimate approximation in the case of lithium ions making impacts with mercury atoms, since the mass of the atom is twenty-nine times the mass of the ion. It is however not valid when the mass of the ion is of the same order or greater than the mass of the atom. If M_1 is the mass of the ion and M_2 the mass of the gas atom or molecule, conservation of energy and momenta give for the scattering angle ϕ as a function of the angle of impact θ,

$$\phi=\cot^{-1}\left[\frac{M_1}{M_2}\csc 2\theta-\cot 2\theta\right], \qquad (1)$$

and for the fractional loss of velocity of the ion,

$$\frac{\bar{c}-c}{\bar{c}}=1-1/(\cos\theta+\sin\phi\cot\theta). \qquad (2)$$

From Eq. (1) and its derivative, the maximum scattering angle can be found, namely:

$$\phi_{(\max)}=\cot^{-1}\left(\left(\frac{M_1}{M_2}\right)^2-1\right)^{1/2}. \qquad (3)$$

The maximum scattering angle for caesium in hydrogen is 51′–46″; for caesium in helium 1°–31′; for sodium in hydrogen 5°; for caesium in argon 17°–10′.

In the apparatus used by the writer the slits were 3×1 mm and the semicircular path from the first to the second slit was 112 mm. The maximum displacement of the once-scattered ions in the plane of the second slit is therefore: for caesium in hydrogen 1.71 mm; caesium in helium 3.4 mm; sodium in hydrogen 9.9 mm, and caesium in argon 35.6 mm.

The statistical distribution of the once-scattered ions in the plane of the second slit is determined by:

(1) the equation between ϕ and θ;

(2) the fact that collisions are equally probable at all points in the path;

(3) the probability of a collision occurring between θ and $\theta+\Delta\theta$ is given by $p=\sin 2\theta\Delta\theta$;

(4) In a constant magnetic field, the proportional decrease in the radius of curvature of the path is equal to the proportional decrease in velocity.

When the range of scattering angle is small, due to the large ratio of M_1/M_2, the pattern produced by the scattered ions cannot be calculated on the assumption that the ions are all scattered on the center line of the stream. By dividing the ion stream into elementary streams and the normal plane at the second slit into elementary areas, the distribution of the ions over the plane of the second slit is given by the summation of the contribution of each of the stream elements to each area element.

A single distribution function involving all the above factors has not as yet been found. However, a close approximation of the distribution of the scattered ions can be obtained by graphic methods. In this manner the proportion of once-scattered ions that will fall on an area 3×1 mm adjacent to the second slit has been determined. It is for caesium in hydrogen 14%; caesium in helium 11%; sodium in hydrogen 6.5%, and caesium in argon 1.6%. When the magnetic field is increased so that the undeviated ions just fail to pass the second slit, the above proportion of once-scattered ions will pass through the

[3] I. W. Cox, Phys. Rev. **34,** 1426 (1929).

slit and register as current to the electrometer. In all cases but that of caesium in argon this proportion is sufficient to give a measurable current. No current was however observed. The slight evidence for sodium in hydrogen occurs for ions that have had, on an average, many more than one collision.

The failure to find small angle scattering by the method used would indicate that the collisions between the ions and the gas molecules or atoms are not governed by the simple assumption of the kinetic theory. (1) The force between the ion and the molecule may be a function of the distance, as indicated by Cox. This would increase the proportion of ions scattered at very small angles but would not affect the maximum scattering angle. (2) The collisions may not be perfectly elastic, part of the energy being converted into radiation. (3) The collision may involve something analogous to friction, resulting in a spin of either the molecule, the ion, or both.

Further experiments are needed which will determine the distribution in angle of the scattered ions and the loss of velocity for different angles of scattering. From the results of such experiments one may expect more definite information as to what happens when a moving ion comes close enough to a relatively stationary atom or molecule to suffer a change in the direction and magnitude of its velocity.

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April 5, 1930.

Certain Effects Accompanying Electron Diffraction

Results on electron diffraction by a copper crystal, for normal incidence on a (100) face, have previously been reported by the writer.[1] With two exceptions, all of the expected diffraction beams which are the x-ray analogues in the two principal azimuths, and in the range below 250 volts were found. In addition, 20 sets of beams were found, 12 of which satisfy the conditions required by a wave of one-half the length given by $\lambda = h/mv$, or by a double grating spacing. It was pointed out that these beams must be due to the structure of the crystal since most of them appear in the (111) azimuth. These beams appeared not to be due to gas. Hendricks[2] has suggested that these "additional" beams are best accounted for by assuming a simple-cubic surface structure with the dimensions of the face-centered structure, and that those "additional" beams not accounted for by this arrangement may be some which have their maximum development in some minor azimuth closely adjacent to the ones in which observations were made. The structure suggested by Hendricks had previously been considered, but did not appear feasible at that time, since the azimuths of the beams not accounted for by this arrangement had been checked and found to be the same as the azimuths in which observations were made. However, there is still the possibility that the "additional" beams may consist of more than one type and that more than one hypothesis will be necessary to account for all of them. As Hendricks pointed out, if the simple-cubic structure is present, then reflection from other possible crystal planes, such as (521) should occur. A search for such beams should then be of value in deciding this question.

During the past several months the measurements above described have been repeated for a new crystal made of exceptionally pure copper. The crystal was made by slowly lowering the molten copper, contained in a pure graphite mold, through a temperature gradient in an atmosphere of hydrogen. The results obtained with the second crystal are in accord with those previously obtained with the first crystal. These results were obtained after outgassing the crystal in a high vacuum for many hours at such red-heat temperatures that considerable copper evaporated from the surface of the crystal. Wolf[3] has recently obtained results which confirm the above observations. For the second crystal *all* of the expected diffraction beams in the two principal azimuths and in the region below 325 volts have been observed. A search for the

[1] H. E. Farnsworth, Phys. Rev. **34,** 679 (1929).

[2] S. B. Hendricks, Phys. Rev. **34,** 1287 (1929).

[3] Karl Wolf, Private communication.

(521) beam above referred to showed it to be present, and hence confirms the hypothesis of a simple-cubic structure.

After obtaining the above observations, the second crystal was then heated at temperatures considerably higher than those previously used, in fact, so near the melting point that in about 10 minutes sufficient copper evaporated from the crystal to make the surrounding glass tube practically opaque to visible light. After 30 minutes of heating at this temperature, with one exception, the "additional" beams occupying the positions required by the simple-cubic structure had decreased in intensity to about 10 to 20 percent of their former values so that only the stronger beams were observable. However, further heating for periods of several hours at the higher temperature failed to further decrease the intensity of these stronger beams. (The crystal has been outgassed at various red-heat temperatures for about 35 hours.) It is thus obvious that these "additional" beams are due to a surface structure. Exposing the crystal while red hot to pressures of hydrogen up to 2 mm Hg failed further to decrease the intensity of these "additional" beams. Hence if this surface structure consists of gas, the last traces of it are much more difficult to remove than in the case of a nickel surface, as found by Davisson and Germer.[4] There is still the possibility that this surface layer is composed of copper atoms, the thickness of which is a function of heat treatment. Very recently the crystal has been exposed to the atmosphere for several days. Then, subsequent to moderate heating at red heat in a vacuum for only a few minutes, it was found to give the same diffraction pattern as originally. With further heating the surface appears to be quickly brought back to its final state, although complete observations on this point have not yet been obtained. This result substantiates the possibility of a gas or oxide layer.

During the course of the above observations certain beams have been found which require a refractive index of unity. A search for other weak beams of this nature reveals a whole series of such beams which accompany the intense diffraction beams as satellites. In many cases these satellites are so close to the main beams that they are not completely resolved, and hence are not observed by the usual method of taking colatitude curves for various primary voltages. In these cases their presence is detected by varying the primary voltage in small steps, and measuring the current to the Faraday collector, whose angular position is adjusted for the maximum of the beam at each reading, while the total primary current is held constant for the entire set of observations.

In the (100) azimuth the satellites which accompany the 4 first-order beams below 325 volts all occur within 2 volts of the theoretical values for unit refractive index; that of one second-order beam occurs within 11.9 volts; that of the other second-order beam is missing. In the (111) azimuth, the satellites of 3 first-order beams are within 2.7 volts of theoretical values; that of the other first-order beams below 325 volts is within 7.3 volts; those of 2 second-order beams are within 5 volts; that of the other second-order beam is within 19.5 volts; that of 1 third-order beam is within 5 volts. The intensities of the satellites are between 10 and 20 percent of those of the main diffraction beams at the lowest voltages, and decrease to an unmeasurable amount at about 325 volts.

It is significant that with but one exception all of the first-order beams fall well within the observational error of the required value for unit refractive index. For the exceptional case in which the voltage difference is 7.3, it should be pointed out that the voltage of the main beam which the satellite accompanies is also several volts from the expected position, indicating an error of the same sign as that of the satellite, and it is the corresponding beam in the second-order whose satellite differs by 19.5 volts from the theoretical value. The voltage of this second-order main beam is also several volts from the expected position, indicating an error of the same sign as that of the satellite. Satellites of the higher-order beams are less certain, but since the higher-order beams are relatively weak and occur only at the higher voltages, this may perhaps be expected. Although the satellites are not present until after a certain amount of red-heat treatment of the crystal, they were observed previous to the final rigorous heating at temperatures very near the melting point. In fact, at least two of the beams obtained with the first crystal are of this type.

[4] Davisson and Germer, Phys. Rev. **30**, 705 (1927).

The satellites are as sharp in voltage and colatitude angle as the main diffraction beams, and are not confined to large colatitude angles. Hence, they are not due to a two-dimensional surface grating. Two possibilities suggest themselves. First: a surface contraction of the crystal lattice. Lennard-Jones and Dent[5] have computed the contraction of the lattice at the (100) boundary of crystals of the NaCl type. They found that the contraction is confined almost entirely to the top layer, and is only of the order of 5 percent. Further, they obtain a decrease in the interatomic spacing in the surface layer of the order of 5 percent. Thus, on the basis of these computations, the depth contraction would be insufficient to account for the shift of some of the beams, and the decrease in the interatomic spacing in the surface layer would produce a marked displacement of the beams from the plane grating lines on which they are found. In addition, the contraction necessary varies from 17.5 percent for the lowest voltage beams to less than 5 percent for the higher voltage beams, and there is no evident reason why a contraction should be such as to make the apparent refractive index exactly unity. Second: a penetration of the incident electron through several layers of the crystal before its velocity is appreciably altered under the action of the inner potential of the crystal. This view is, of course, contrary to the present conception, and, while it would account for observations similar to the above for a single lattice, there is some uncertainty in explaining on this basis the presence of the above satellites previous to the removal of most of the surface lattice.

Additional observations which, however, appear in accord with this view are the following. Simultaneously with the weakening of the "additional" beams requiring a simple-cubic structure, there appeared a new set of beams on the $\frac{1}{2}$-order lines in both the (100) and (111) azimuths indicating that the surface layer on the crystal was changing in structure from a single-spaced simple cubic to a double-spaced face-centered cubic. Further, the positions of these latter beams are such as to require a refractive index of approximately *unity* while those due to the simple-cubic structure require a refractive index *greater than unity*. There is also a shift in the voltage of the beams due to the simple-cubic structure as their intensity decreases, such as to decrease the refractive index. Observations on the structure formed by the condensation of hydrogen on the crystal show that hydrogen forms in two different lattices depending on the pressure of the hydrogen while the lattice is formed. At small pressures (less than 0.5 mm Hg) a relatively thin double-spaced face-centered structure is formed; at larger pressures (2 mm Hg) a thicker single-spaced simple-cubic structure takes its place. The beams for the first structure require a refractive index of approximately *unity* while those of the second structure require one *greater than unity*. This second structure is extremely unstable and reverts to the first structure in the course of a few minutes under the bombardment of the low-velocity primary electrons. The presence of hydrogen on the surface does not decrease the intensity of the main diffraction beams as is the case for air.

A careful examination of the observations on the "additional" beams requiring a simple-cubic structure shows in some cases the presence of satellites of these beams requiring a refractive index close to unity.

Taking into account the various types of diffraction beams outlined above, there are still a few very weak beams observed with the first copper crystal which cannot be classified. It was found, however, that during the course of the heat treatment of the second crystal, most of these weak beams disappeared before the decrease in intensity of the "additional" beams requiring a single-spaced simple-cubic structure occurred. They may, therefore, be attributed to a slight trace of some other form of surface structure which was not identified.

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Department of Physics,
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April 19, 1930.

[5] Lennard-Jones and Dent, Proc. Roy. Soc. **121A**, 247 (1928).

Absorption and Emission Spectra in the Region λ600–1100.

Lyman discovered the resonance series of helium several years ago. I have repeated his work and in addition have studied the ultraviolet light emitted by helium, and by helium mixed with other gases. The following is a preliminary report of many new

phenomena observed.

A region, λ600–λ1000, of very strong continuous light has been discovered in helium. This is best observed in a condensed discharge. The short wave-length limit of the continuous source found by Lyman and Schumann is about λ900. The new continuous spectrum is the only one known in the region λ600-900. This continuous spectrum is an isolated one, and on this account its second order is also very useful. With this light as a background, absorption bands have been observed in this region. Among these is a new system of bands in hydrogen. The 0-0 band of this system is λ842, and the electronic levels concerned in its production are the normal level and a new one 14.7 volts above it. A progression of eight bands have been observed. These new bands are much stronger than the *A-B* and the *A-C* absorption bands previously found by Dieke and Hopfield.

Strong absorption bands in this region have been obtained also in nitrogen and oxygen. I have not yet examined any of these in great detail. There are several scores of them forming perhaps many systems. They are especially interesting for in this region of high frequency one expects to find bands with high electronic quantum numbers, bands concerned with double electronic transitions and possibly even bands of ionized molecules.

An examination of a small part of these spectra shows clearly six bands in a region unmixed with others. They are λλ722, 694, 682, 675, 671 and 669. These bands form approximately a Rydberg series. Since they occur in absorption they are probably due to electronic transitions from the normal level, and their limit of convergence, 18.58 volts, is the ionizing potential of the molecule. The form of the series, the spacing of the bands and the experimental conditions all point to helium (He_2) as the source of these bands. From the above measurements the effective quantum number of the lowest level is 0.853. This is one unit less than the value of the number for the $2S^1\Sigma$ term of helium found by Curtis and others.

The resonance series of the helium atom discovered by Lyman has been extended to nine members which is two more than were observed by him. I have observed the first line self-reversed and lying in what appears to be a strong band several angstroms wide. This resonance line was obtained in five orders and the fourth and fifth orders have been photographed against iron standards. Its wave-length measured in the fifth order is λ584.358 I.A. reduced to vacuum. This value is about 0.04A lower than that given by Lyman. The band at λ600 was observed under certain conditions, and there have been found also some new emission bands in this region probably due to helium.

In a mixture of helium and hydrogen thirteen members of the Lyman series have been observed. This more than doubles the known length of the series. Two very interesting things are evident from the spectrograms. One is that the Lyman series shows a much smaller intensity gradient when produced in an excess of helium than when produced with only atomic hydrogen present in the discharge tube. The other is that in an excess of helium an anomalous intensity occurs in the line λ972 of hydrogen. This line, the third member of the series, is much weaker than the lines near it. It is in fact only as strong as the sixth line. If this anomaly has its source in the four-quantum state of the atom one would expect a similar weakening of H_β of the Balmer series. This phenomenon is now being investigated. If this found to be true in the visible series it would be a parallel to the case of the spectra of *M*-type stars in which H_γ is weaker than H_β.

JOHN J. HOPFIELD
University of California, Berkeley
April 20, 1930

BOOK REVIEWS

Technische Mechanik. L. FÖPPL, Pp. 189+x, figs. 117. Akademische Verlagsgesellschaft, Leipzig, 1929. Price bound, RM 19.75.

This book constitutes part 2 of mechanics in the "Handbuch der Experimentalphysik," many references being made to A. Hass' "Mechanik der Massenpunkte und der starren Körper" which appeared as part 1.

The text contains an elementary presentation of the simpler problems of applied mechanics, the author's endeavor being to impart to the reader a clear understanding of the principles underlying the subject rather than to furnish him with information alone. Although the treatment is quite elementary, the author uses the calculus freely and introduces scalar and vector products without much explanation of their meaning. The topics treated are statics, kinematics, dynamics of particles, dynamics of groups of particles, dynamics of rigid bodies, impulse, friction, in the order given. The book is exceptionally well illustrated by line drawings and halftones.

LEIGH PAGE

Intermediate Dynamics and Properties of Matter. R. A. HOUSTOUN. Pp. 138, figs. 139. Longmans Green and Co., London, 1929. Price $1.25.

This text constitutes the first part of a series on Intermediate Physics of which the sections on Heat, Light and Electricity and Magnetism have aready been published. Elementary algebra and trigonometry are used, but no calculus. The topics are well selected and clearly treated, although one may object to the time-honored but meaningless definition: "The mass of a body is the quantity of matter in it." A number of simple problems are placed at the end of each of the twelve chapters, and a list of Oxford and Cambridge Schools examination questions together with answers to problems at the end of the book.

LEIGH PAGE

Foundations of Potential Theory. O. D. KELLOGG. Pp. 384+ix. Julius Springer, Berlin, 1929. Price bound RM 21.40.

This excellent treatise on potential theory is based on two courses, one elementary and the other advanced, which the author has given at Harvard. In the first quarter of the book the subject is treated in a fairly elementary manner, with applications to gravitational theory, electrostatics, magnetostatics and the flow of heat. It is, perhaps, unfortunate that the author feels constrained to follow the convention of defining the potential in a gravitational field as the negative of the potential energy per unit mass, as this procedure necessitates a revision of the definition when elements which repel as well as attract are taken into consideration, causing needless confusion on the part of the student as to the proper sign to be used. The author avoids the use of vector notation, writing (X, Y, Z) for the vector whose rectangular components are represented by the three capitals, and employs the notation, grad, div, curl in preference to Gibbs' significant symbols.

The last three-quarters of the book is more mathematical in character. The restrictions on the validity of Gauss' and Stokes' theorems are carefully examined and these theorems are proved under broad conditions, a study is made of Laplace's equation with applications to electrostatics, and the development of functions in series of spherical harmonics and in Fourier series is investigated. The last part of the book is concerned with the establishment of existence theorems, particular attention being paid to the Dirichlet problem and its investigation by the use of integral equations.

Exercises in the form of problems are interspersed through the text, and an index and a brief bibliography are appended. The book should prove very valuable, particularly to those who are interested in the rigorous development of the subject of potential theory.

LEIGH PAGE

Atoms, Molecules, and Quanta. ARTHUR E. RUARK AND HAROLD C. UREY. First edition, 1930. Pp. xvii+765+25 (indices), 6×9 in. McGraw-Hill Book Co., New York, Price $7.00.

This is the second book of the International Series in Physics, F. K. Richtmeyer, Consulting Editor, which was inaugurated last fall by the "Quantum Mechanics" of Condon and Morse. It bids fair to become the long needed prototype of Sommerfeld's Atombau for the English language. Written with a double purpose, the first part (Chap. I–XIV) is intended to satisfy the needs of those who are approaching the study of atomic and molecular structure for the first time, while the latter part attempts to furnish the initiated with an up-to-date account of the theoretical and experimental aspects of quantum mechanics.

The chemical influence of one of the authors is strongly suspected (and approved) by the reviewer in reading the significant statement in the preface, "On the other hand, a very large number of physicists and chemists do not wish to eliminate models from their modes of thought, nor to rely entirely on mathematical connections between their observations. In the past these models have consisted of particles, moving on selected orbits. . . . . It is only human nature to construct a new picture of a hidden mechanism as soon as an old one is discarded." It is with this view point that the authors devote the first eleven chapters to a complete discussion of the orbital theory of the atom. After a historical development of the fundamentals of atomic theory, with a careful description of experimental details, a very good chapter entitled "Review of Dynamical Principles" is inserted. This is distinguished by many clarifying illustrative examples. Then follows a consideration of hydrogenic atoms and their spectra. It is to be regretted that the authors have not seen fit to adhere to the Gibbs system of vector notation and have preferred the German. Chapter VI on general theorems of the older quantum theory (such as the correspondence principles, the adiabatic principle and a justification of the Bohr quantum conditions) is a parenthesis interrupting the continuity of the treatment of spectra and would have been better placed in the appendix along with relations between average kinetic and potential energies, quantum integral evaluation, phase and group velocities, mathematical manipulation of functions arising in the wave mechanics, Maxwell's equations, Larmor's theorem, radiation from a moving charge and the relativity transformation. The subsequent chapters then develop spectroscopic theory, the climax occurring in chapter X where the general theory is illustrated by an actual typical multiplet spectrum (Cr). The theory of molecular spectra is expounded in Chapter XII, which comprises some eighty pages. The discussion of this subject is divided into three parts, the first dealing with infrared spectra (18 pages), the second with electronic bands (50 pages) and the last with spectra from polyatomic molecules. The discussion of the spectra of diatomic molecules is quite satisfactory. A paragraph is devoted to the relation between the different systems of nomenclature (five in addition to that of the authors) now in use. The inclusion of polyatomic spectra is especially welcome, as this is the first serious attempt at a critical treatment in any treatise beyond the statement that they are too complicated and that too little is known concerning them. The first or elementary part of this book winds up with a presentation of the present status of critical potential measurements and experiments involving collisions of the second kind.

The second part of the book starts off with a chapter on wave mechanics, followed by its application to hydrogenic atoms. An intelligible chapter is then devoted to an exposition of matrix mechanics, which it seems we must understand in spite of the almost insurmountable difficulties experienced in obtaining important results (without the aid of Schrödinger's method), because of the persistence of theoretical physicists in interjecting surreptitiously into their discussions the phrase, "The matrix components of such and such." A couple of paragraphs are also given of Dirac's formulation of quantum dynamics and his theory of q numbers. The general theory of quantum dynamics is next developed in its relation to Heisenberg's uncertainty principle. The transformation theory of Dirac is also given. Chapter XIX takes up the conditions occasioned by equivalence degeneracy and discusses He, H_2 and H_2^+ and the symmetry properties of diatomic molecules consisting of equivalent nuclei. As most of the material in chapter XX on spectral intensities is derived from classical theory, that involving quantum mechanics being merely quoted without proof, it seems that this chapter is out of place and should have been presented earlier in the first part along with spectroscopy,

perhaps immediately following the chapter on band spectra. The book ends with a presentation of the Davisson and Germer effect, and allied matters.

The authors have not discussed the quantum mechanical aspects of radioactivity, statistics, valence, nor group theory. The book is well illustrated, but tables of data for the use of the experimental worker are rather scarce. This, however, is probably beyond the scope of such a treatise. Although the arrangement in places is not ideal, the wealth of material seems to be well indexed and the book is therefore highly recommended for reference use in clearing up knotty theoretical points.

D. S. VILLARS

Lehrbuch der Chemischen Physik. A. EUCKEN. Pp. xvi and 1037, 250 figures. Akademische Verlagsgesellschaft, m.b.H., Leipzig 1930. Price bound RM 56.

Eucken's book which appeared in its first edition in 1922 with 492 pages, has grown with this third edition into a volume of double the size and has changed its name from a text-book in physical chemistry to a text-book in chemical physics, making the emphasis on the physical side even stronger than it had been in the first edition. A number of features which were characteristic of the first edition have survived. Among them is the general plan which consists in dividing the book into two parts, the first presenting the phenomena from the standpoint of the theory of heat and occupying about 600 pages. The second, under the title "Structure of Matter," occupies the rest.

The first part is divided according to subjects. Each chapter falls then into usually four parts: presentation of the experimental facts, treatment with the method of thermodynamics, explanation with the help of kinetic theory and practical applications. In the whole treatment of the first part it is characteristic that the modern views are introduced rather early. But as a concession to the reader the somewhat crisp statements of the first edition have been elaborated and perhaps from the standpoint of the theoretical physicist lose something of their original precision.

The first chapter is an introduction presenting the first and second law, the general ideas of the kinetic theory, Maxwell's distribution law and even the statistical interpretation of entropy. The Reviewer thinks it a pity that Eucken has relinquished the name of "free energy at constant pressure" for $U-TS+pv$ which he had adopted in his first edition in agreement with Lewis and Randall and has gone back to the historical name introduced by Gibbs.

The following chapters treat ideal gases, then solid bodies. In this latter chapter a rather full treatment of the specific heat of solids is given and accordingly the quantum theory of specific heats is introduced already here. The next chapter on real gases gives more concerning the corrections for the reduction to the ideal gas state than is usual. Chapters on liquids and on the laws concerning the change of state follow in which the empirical relations, the new thermodynamics, kinetic theory and general statistics are discussed very completely. The next chapters deal with the more chemical equilibria, first for ideal gases then for condensed solutions of all types. It is in these chapters and the following where the growth compared with the first edition is largest. Formerly Eucken had referred the reader for these more conventional subjects to other books but since this time even these old-fashioned questions have advanced so much that an extended treatment seems necessary. This applies especially to the theory of strong electrolytes which was almost completely missing in the first German edition, but had been added to the English translation by Jette and La Mer. An almost completely new chapter follows on surface phenomena, dealing with adsorption and the highly important question of surface potentials.

The next three chapters treat of irreversible processes, namely diffusion, electrical phenomena, among which are to be mentioned a treatment of electrokinetics which play such an important part in biology, and finally on chemical kinetics. It is in this last subject that the American reader will feel some gaps. Especially he will be astonished that the name of H. S. Taylor does not occur.

The whole treatment in this first part is admirably suited to teach the subject in its many sides. There are a number of small points where the opinion of the Reviewer differs with that of the author in this as well as in the second part.

The subject of the second part makes the task of the writer particularly difficult, because the more intricate problems of theoretical physics, the theory of line and especially band spectra have gained a large importance for the chemists as the only method of gaining a knowledge of some molecules which can not be prepared in large amounts. Accordingly one must make available to the physico-chemist the methods to analyze spectra without forcing him to go through all the difficult calculations of the theory. In this Eucken has been highly successful.

After an introduction giving the general properties of electrons and nuclei and radioactivity, he treats first the general quantum principles for emission and absorption of energy and then he goes on to describe the characterization of optical and x-ray spectra, including the new quantum theory but without giving too many mathematical details. The Pauli principle leads to the periodic system and a description of the possible spectral terms.

The next chapter deals with the properties of molecules, their spectra, the application to specific heats—the hydrogen problem is included. The calculation of the heat of dissociation concludes this subject. There is then a chapter on optical refraction and polarization in which field the measurement of dipole-moments has given considerable insight into the structure of organic molecules. Finally the nature of the chemical valence is discussed, the unipolar bond is explained according to the new quantum theory (Heitler and London), while for the polar compound the older theory of Kossel is given. The properties of crystals, determination of their structure and the question of the forces holding them together are treated next with mention of the theory of metals at the end.

Summing up, the book is a treatment of the most interesting chapters of physics, written for chemists who have the necessary endurance to master the difficulties which can not be avoided.

KARL F. HERZFELD

Inorganic Chemistry for Colleges. WILLIAM FOSTER. Pp. viii+837. Figs. 212. D. Van Nostrand Company, New York, 1929. Price $3.90.

Since the author has written this book for students of second year chemistry, the treatment is much more complete and comprehensive than most of the text-books for college chemistry. The author follows a different yet worthwhile arrangement of subject matter, and divides the book into four parts: I. Introduction, II. Non-metals, III. Metals, IV. Supplementary—carbon compounds.

It is in Part I that the greatest departure from standard practice occurs. Following an excellent historical introduction the author considers such fundamentals as the laws of chemical combination, the atomic theory, the gas laws, the kinetic theory, and the internal structure of crystals. These are well presented and very nicely illustrated. Radioactivity and the radioactive elements are then studied in some detail so that an experimental foundation is laid for the study of atomic structure and the classification of the elements. This concludes the first section of the book.

The second part of the book covers in a fairly complete way the chemistry of the non-metallic elements. In addition the subject of solutions follows the chapter on the chemistry of water. Ionization, ionic theory, the properties of acids, bases, and salts as well as oxidation and reduction are also considered in this section which is concluded by a chapter on colloid chemistry. In the work on colloids, the author makes the mistake of using $\mu\mu$ for $m\mu$. This is one of the very few errors in the book. The third section deals with the chemistry of the metallic elements together with a chapter on electrochemistry. As stated by the author, part four is supplementary and may be used or not as the teacher sees fit. It is an introduction to the study of organic chemistry. Ten pages of well chosen problems appear at the end of the book as well as a useful appendix of tables.

The book as a whole is very well written and should prove valuable as a text for second year students. The presentation of radioactivity and atomic structure before consideration of the chemistry of the elements is being advocated more and more by teachers of college chemistry. The author places his book in the forefront of those adopting this style of presentation. The format of the book is good and it is excellently illustrated.

L. H. REYERSON